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- 455 2\* }  
 463 6\* } for "10-acetyl-5:10-dihydrophenarsazine" read "10-acetoxy-  
 464 1 } 5:10-dihydrophenarsazine."  
 1032 15 for "Thomson" read "Thomsen."  
 1042 20\* The work to which reference is made in the sentence beginning  
 "It was after his return to South Kensington. . . ." was  
 carried out at the Government Laboratory, with A. G. Francis  
 as Sir Edward Thorpe's collaborator. The results were pub-  
 lished in 1910.  
 1043 13 for "Government Chemists' Department" read "Department of  
 the Government Chemist."

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- 1896 14\* for "Hertz" read "Herty," and for "1892, 14, 107" read  
 "1896, 18, 290."





# JOURNAL

OF

## THE CHEMICAL SOCIETY.

### I.—*The Action of Hydrogen Sulphide on a Neutral Solution of Potassium Permanganate.*

By HORACE BARRATT DUNNICLIFF and SUKH DAYAL NIJHAWAN.

WHEN a slow current of hydrogen sulphide is passed through a 1% solution of potassium permanganate, the purple solution becomes brown and a white deposit of sulphur appears round the delivery tube. After a short time, a greyish-brown solid separates without appreciable rise in temperature; this slowly changes first to a yellow mixture of hydrated manganese dioxide, manganese sulphide, and sulphur and finally to a pink precipitate of manganese sulphide containing much sulphur, the temperature rising rather more than  $10^{\circ}$ .

The course of the reaction was investigated in stages.

When a solution of potassium permanganate was shaken with hydrogen sulphide solution, a brownish-black precipitate of hydrated manganese dioxide and sulphur formed immediately; the faintly alkaline filtrate contained unchanged permanganate. The precipitate was well washed by decantation with air-free water, and the manganese dioxide in it was estimated by determining the amount of chlorine it liberated from hydrochloric acid. The liquid left over from this estimation was treated with sodium carbonate, and the total manganese weighed as  $Mn_3O_4$ . Three estimations gave values of 1:3.8, 1:3.1, and 1:2.7 for the molecular ratio  $MnO:MnO_2$ , showing that the manganese is only partly precipitated as hydrated dioxide.

Through solutions of potassium permanganate of various concentrations hydrogen sulphide was passed until the whole of the manganese was converted into sulphide. The precipitate was filtered off, and the manganese present in it as sulphide was estimated by two methods: (1) The sulphide was extracted with dilute hydrochloric acid, the solution filtered, and the manganese precipitated

as carbonate and weighed as  $\text{Mn}_3\text{O}_4$ . Recovery = 99.8% of theory. (2) The sulphide containing free sulphur was ignited and so converted into  $\text{Mn}_3\text{O}_4$ . Recovery = 99.9% of theory.

The yellow filtrate, which contained colloidal sulphur and was faintly alkaline to phenolphthalein, was freed from hydrogen sulphide by shaking under reduced pressure, and kept in a vacuum desiccator. The sulphur deposited was filtered off and the liquor, now colourless, was left in a vacuum desiccator over a dehydrating agent for some days. Needle-shaped crystals of potassium thiosulphate and rhombic crystals of potassium sulphate grew in it as it became concentrated. The filtrate did not contain polythionates, sulphide, or sulphite. To test for polythionates, the filtrate was examined qualitatively by the tests given by Takamatsu and Smith (J., 1880, 37, 592), Bassett and Durrant (J., 1923, 123, 1279), Gutmann (*Ber.*, 1905, 38, 3277; 1907, 40, 3614), Sander (*Z. angew. Chem.*, 1915, 28, 9; 1916, 29, 11, 16), and Riesenfeld and Feld (*Z. anorg. Chem.*, 1921, 119, 225) in comparison with control thionate solutions of known concentrations.

It was shown that hydrogen sulphide has no action on thiosulphates by passing the gas through standard solutions of sodium thiosulphate at various temperatures; the excess was removed under diminished pressure, and the solutions were titrated against iodine solution. The absence of colloidal sulphur was demonstrated by negative results on the addition of electrolytes and with the cataphoresis test.

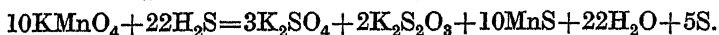
*Estimation of the Compounds produced at Various Stages in the Action of Hydrogen Sulphide on Potassium Permanganate.*

In all cases, the excess of hydrogen sulphide was removed by means of a suction pump or by the addition of lead carbonate.

(1) *Estimation of the Products of the Complete Reaction.*—The manganese is quantitatively precipitated as sulphide (see above).

The sulphate in the filtrate was estimated as barium sulphate, the precautions advised by Taylor (*J. Soc. Chem. Ind.*, 1923, 42, 294r) being taken but acetic acid being used instead of hydrochloric acid as suggested by Müller (*Bull. Soc. chim.*, 1916, 19, 8) when sulphates are being estimated in presence of thiosulphates. The thiosulphate in the filtrate was estimated iodometrically, the solution being first acidified with acetic acid (Müller, *loc. cit.*). The mean of several results gave 61.86% of potassium recovered as potassium sulphate and 38.16% as potassium thiosulphate. The sum of these values, 100.02, shows that the whole of the potassium is eventually recovered in these two forms. Practically the same values were obtained from experiments at temperatures ranging from  $-3^\circ$  to

+76°. The values approximate to three molecules of potassium sulphate to two of potassium thiosulphate, and the result, when the reaction is complete, can be summed up in the equation



At the end of the reaction the solution is alkaline and, if it is not acidified before the titration with iodine, the values for the thio-sulphate are always high. Control experiments showed that the lead carbonate used to remove the excess of hydrogen sulphide from the solution has no action on the thiosulphate. The thiosulphate found in a solution (4.170 g. per litre) which had been treated with hydrogen sulphide, shaken with lead carbonate, filtered, and then titrated against iodine was 4.164; 4.167; 4.170; and 4.165 g. per litre.

(2) *Investigation of the Mechanism of the Reaction by a Study of Two Intermediate Stages.*—Hydrogen sulphide was passed through the solution until the hydrated manganese dioxide was converted into a dirty yellow, granular mass. The values then found for potassium recovered as sulphate and as thiosulphate were 59.61, 58.54% and 34.32, 32.45%, respectively, of the total potassium. Since the sum of these values (93.93, 90.99) does not account for all the potassium present, it appears that some other sulphur compound of potassium is first formed which is subsequently decomposed by hydrogen sulphide into potassium sulphate and thiosulphate; the average final values for potassium recovered as sulphate and as thiosulphate were 61.66% and 38.27%, respectively (sum, 99.93). This compound may be one (or more) of the polythionates, for penta-, tetra-, and tri-thionates are known to be thus decomposed by hydrogen sulphide (Debus, J., 1888, 53, 328) and the authors have shown that dithionates slowly undergo a similar change in presence of this gas.

*Identification of the Compounds formed in Solution when the Manganese is precipitated as Hydrated Manganese Dioxide.*

A solution of potassium permanganate was shaken with successive small quantities of half-saturated aqueous hydrogen sulphide until the brown colour just disappeared. (When this was done carefully with standard solutions, it was not possible to obtain a definite end-point.) The filtered liquid, which was faintly alkaline, contained sulphate, thiosulphate, and dithionate, but no sulphide, sulphite, penta-, tetra-, tri-thionate, colloidal sulphur or manganese. In view of the difficulty of testing for thionates in presence of one another, the tests given (p. 2) were performed both on the filtrate and on control solutions of thionates of known concentrations.

The distinction between thiosulphate, dithionate, and trithionate was made as follows : The solution decolorised iodine solution and gave a black precipitate with silver nitrate. (The solution gave no precipitate when warmed with hydrochloric acid. This was due to the low concentration of the thiosulphate.) Dilute aqueous potassium permanganate added to the solution was first bleached (thiosulphate), then a blood-red coloration developed, and brown hydrated manganese dioxide was slowly precipitated. This suggested the presence of tri- or di-thionate. The filtrate from the precipitation of the sulphate by barium chloride was warmed with dilute hydrochloric acid; sulphur dioxide was detected, but sulphur was not deposited. Sulphate was detected in the solution (distinction from thiosulphate). Trithionates give sulphur dioxide, sulphate, and sulphur. Dithionates give sulphur dioxide and sulphate only. In dilute solutions the sulphur may not be precipitated. Mercuric chloride gives a yellow precipitate with trithionates, but does not react with dithionates. With this reagent, the filtrate gave a white turbidity. This is given by thiosulphates in very dilute solution. This suggests the absence of trithionates and the presence of thiosulphate. Ammoniacal silver nitrate had no action on the filtrate. A trithionate would have given a brown coloration.

*Action of Hydrogen Sulphide on Hydrated Manganese Dioxide.*

The blackish-brown precipitate of hydrated manganese dioxide obtained by the action of dilute aqueous sodium hypochlorite on a solution of manganous chloride, after being thoroughly washed with water, was free from alkali, chloride, and hypochlorite. It was suspended in water, through which scrubbed hydrogen sulphide was then bubbled for some time. A large proportion of the dioxide was converted into manganese sulphide contaminated with sulphur, and the solution, which was neutral to phenolphthalein, contained manganese as sulphate and thiosulphate. Ordinary dry A.R. manganese dioxide, when suspended in water and treated with hydrogen sulphide, gave the same results, and so also did hydrated manganese dioxide formed by the action of hydrogen sulphide on potassium permanganate and washed free from sulphate and thiosulphate and until the washings gave no indication of alkalinity with phenolphthalein. The presence of dithionate was not definitely proved, but independent experiments showed that manganese dithionate is decomposed by hydrogen sulphide into the sulphate and thiosulphate.

If neutral potassium sulphate was added to the water in which the hydrated manganese dioxide was suspended, the solution, in which manganese could not be detected, became alkaline to phenol-

phthalein and, when hydrogen sulphide was passed into it, the manganese was completely converted into manganous sulphide. The alkalinity was probably due to the adsorption of sulphate ions of the potassium sulphate. This would also account for the alkalinity of the solution in the reaction under investigation.

*Quantitative Estimation of Intermediate Products in the Filtrate.*

A dilute solution of potassium permanganate was treated with half-saturated aqueous hydrogen sulphide in the way described on p. 3, the precipitate was well washed, and the washings and the filtrate were made up to a definite volume. Care was taken that the solution contained no free hydrogen sulphide. In aliquot portions, the sulphate and thiosulphate were estimated as described on p. 2, and the dithionate by Szentpaly-Peyfuss's method (*Z. anorg. Chem.*, 1924, **131**, 203).

TABLE I.

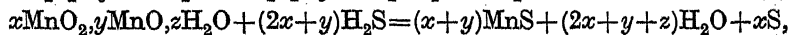
*Estimation of Sulphate, Thiosulphate, and Dithionate in the Filtrate.*

Percentage of the potassium recovered as			Total
sulphate	thiosulphate	dithionate.	recovered.
69.70 (79.72)	4.84 (19.98)	25.06	99.60
79.87 (83.67)	10.27 (15.98)	9.51	99.65
68.08 (78.82)	4.65 (20.76)	26.84	99.57

The potassium is quantitatively accounted for as sulphate, thiosulphate, and dithionate, but the results show variations in the proportions in which the components are present. If it is assumed that the dithionate decomposes quantitatively into sulphate and thiosulphate, the values given in brackets would be obtained for potassium as sulphate and thiosulphate.

The results can be reconciled with the average values of 61.66 and 38.27% found for the potassium recovered as sulphate and thiosulphate, respectively, in the completed reaction (p. 3) as follows. When a large excess of hydrogen sulphide is passed, air is practically excluded from the reaction. Possibly, also, any oxidising action of the hydrated manganese dioxide is confined to the hydrogen sulphide, because dithionates are not oxidised by manganese dioxide. It is suggested, therefore, that the first products of the reaction are potassium sulphate, potassium dithionate, hydrated manganese dioxide, and sulphur; all attempts to stop the action at this stage, however, have failed. The stoichiometric proportions in which the potassium sulphate and thiosulphate are found at the end of the reaction preclude the possibility of potassium dithionate being the only potassium salt first formed. The

second stage of the action may be represented by the equations



and hence the final result is potassium sulphate and thiosulphate in solution and a precipitate of manganous sulphide and sulphur. When the dilute solution is shaken with hydrogen sulphide, air dissolves freely and a part of the dithionate is directly oxidised to sulphate at the expense of the thiosulphate which would otherwise have been formed from the dithionate in the presence of excess of hydrogen sulphide. Excess of hydrogen sulphide thus does the double duty of reducing the dithionate to sulphate and thiosulphate and protecting it from oxidation by dissolved air. In support of this argument, attention is directed to the results on p. 3. These represent a stage intermediate between those for the final values ( $\text{K}_2\text{SO}_4$ , 61.66% ;  $\text{K}_2\text{S}_2\text{O}_3$ , 38.27%) and those given in Table I, i.e., a stage in which the "protecting" action of the hydrogen sulphide has been fully exerted but in which its reducing action has been stopped before completing its work. Assuming the decomposition of the dithionate into sulphate and thiosulphate in the sense of equation (1), the values on p. 3, calculated for the final product, become  $59.61 + (0.4 \times 6.07) = 62.04$  and  $58.54 + (0.4 \times 9.01) = 62.14$  for the percentage of potassium present in solution as sulphate and  $34.32 + (0.6 \times 6.07) = 37.96$  and  $32.45 + (0.6 \times 9.01) = 37.86$  for the percentage of potassium present as thiosulphate.

These results support the argument that the hydrogen sulphide has a protecting and reducing action, since, in the completed reaction, it was used in excess of that required for the first stage and air could have taken little or no part in the reaction.

### *Summary.*

The first products of the reaction between hydrogen sulphide and potassium permanganate in dilute solution appear to be colloidal hydrated manganese dioxide, which quickly coagulates to a gelatinous precipitate; sulphur; and potassium sulphate and potassium dithionate in solution.

When excess of hydrogen sulphide is passed through the solution, the hydrated manganese dioxide is converted into manganous sulphide with the separation of sulphur. The manganous sulphide is first formed as a colloid, which quickly coagulates to pink manganous sulphide. Excess of hydrogen sulphide decomposes the potassium dithionate into potassium sulphate and thiosulphate with the simultaneous formation of sulphur. A portion of the

sulphur is precipitated; the rest is in colloidal solution and is completely precipitated on standing.

The solution is alkaline throughout. This is probably due to the adsorption of the anions of the potassium salts by the hydrated manganese dioxide or manganous sulphide.

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[Received, June 26th, 1925.]

## II.—Preparation of 1-Halogeno-2-nitronaphthalenes and 2-Nitronaphthalene.

By HERBERT HENRY HODGSON and ERNEST KILNER.

2-NITRO-1-NAPHTHYLAMINE is readily obtained from 2-nitro-1-naphthol, which is itself best prepared by the oxidation of 2-nitroso-1-naphthol (Hodgson and Kilner, J., 1924, **125**, 807). For the preparation of large quantities of 4-nitro-1-naphthylamine Morgan and Micklethwait's modification (J., 1905, **87**, 928) of Lellmann and Remy's method is serviceable.

Hydrolysis of aceto-1-nitro- $\beta$ -naphthalide proceeds better with acid than with alcoholic potassium hydroxide (Liebermann and Jacobson, *Annalen*, 1882, **211**, 44), which produces a substantial quantity of 1-nitro-2-naphthol.

By very slow decomposition in the cold in presence of cuprous chloride and concentrated hydrochloric acid, diazotised 2-nitro-1-naphthylamine gives a good yield of 1-chloro-2-nitronaphthalene. Under similar conditions, only poor yields of the corresponding bromo- and iodo-compounds are obtained, which may be due to the preferential formation of naphthalene-1-diazo-2-oxide (compare Friedländer, *Ber*, 1895, **28**, 1951; Morgan and Evens, J., 1919, **115**, 1126). Vesely's electrolytic method (*Ber.*, 1905, **38**, 136) proved unsuitable for the preparation of 1-chloro-2-nitronaphthalene.

These substances all have an extremely irritating action on the skin.

### EXPERIMENTAL.

**2-Nitro-1-naphthylamine.**—A finely powdered mixture of 2-nitro-1-naphthol (5 g.) and ammonium carbonate (3 g.) is made into a paste with concentrated ammonia (10 c.c.) and water (6 c.c.), and heated in a sealed tube at 120–130° for 6 hours. The product when cold is pulverised, and boiled with 200 c.c. of water, aqueous ammonia being occasionally added. The solution, containing the ammonium salt of unchanged 2-nitro-1-naphthol (0.31 g.), is filtered and the solid is dried and extracted with boiling alcohol (150 c.c.).

The extract on evaporation leaves 2-nitro-1-naphthylamine (3.8 g.), which melts at 141°, and at 144° after recrystallisation from alcohol (Lellmann and Remy, *Ber.*, 1886, **19**, 797; 1887, **20**, 872, give m. p. 144°). The substance insoluble in alcohol (about 0.52 g.) does not melt at a high temperature and is probably 2 : 2'-dinitrodinaphthylamine (Found: N, 12.0.  $C_{20}H_{13}O_4N_2$  requires N, 11.7%). An experiment made in an autoclave produced 16 g. of 2-nitro-1-naphthylamine and 1.3 g. of insoluble material from 20 g. of 2-nitro-1-naphthol, 1.8 g. of which were recovered.

**4-Nitro-1-naphthylamine.**—Experiments similar to the above carried out with 4-nitro-1-naphthol indicated an optimum reaction temperature between 140° and 160°. The quantities of 4-nitro-1-naphthylamine, material insoluble in alcohol, and recovered 4-nitro-1-naphthol, respectively, were: (at 120–130°) 0.5 g., —, and 6.8 g. from 8 g.; (at 140°) 2.82 g., 0.24 g., and 1.73 g. from 5 g.; (at 160–165°) 2.94 g., 1.43 g., and 0.2 g. from 5 g. of 4-nitro-1-naphthol. The nitronaphthylamine obtained at 140° melted at 182°, and at 191° after crystallising once from alcohol.

**1-Nitro-2-naphthylamine.**—A mixture of  $\beta$ -naphthylamine\* (1 part), 50% acetic acid (5 parts), and acetic anhydride (1 part) is boiled under reflux for 1 hour; on cooling, aceto- $\beta$ -naphthalide separates in flaky crystals. This product (200 g.) is added in four equal portions to cold glacial acetic acid (250 c.c.), into which, after each of the first three additions, 70% nitric acid (15 c.c.) is run during 1 hour, the temperature being kept at 8–10°. This procedure obviates the stiffening of the reaction mixture which renders Liebermann and Jacobson's process (*loc. cit.*) almost unworkable. After the last addition of aceto- $\beta$ -naphthalide, 25 c.c. of nitric acid are added to the mixture, which is then kept for 2 days. The orange-yellow aceto-1-nitro- $\beta$ -naphthalide that has separated is filtered off and washed with ether (yield 170 g.).

Hydrolysis is effected by boiling a solution of the product (125 g.) in alcohol (500 c.c.) with concentrated hydrochloric acid (125 c.c.) for 4 hours; the treatment is repeated if necessary. The mixture is then poured into 4 litres of cold water and the crude 1-nitro-2-naphthylamine filtered off, dried, and recrystallised from twice its weight of hot alcohol; m. p. 122° (Atterberg gives m. p. 124–125°, and Meldola, 126–127°) (Found: N, 15.0. Calc., 14.9%).

**1-Chloro-2-nitronaphthalene.**—Five grams of sieved 2-nitro-1-naphthylamine are warmed with 30 c.c. of a mixture of 98% sulphuric acid (3 vols.) and water (1 vol.) (*i.e.*,  $H_2SO_4, H_2O$ ). The solution thus obtained is cooled to 0°, stirred, and solid sodium

\* Pinnow's directions (*Ber.*, 1900, **33**, 417) for acetylating  $\alpha$ -naphthylamine give an unsatisfactory result in the case of  $\beta$ -naphthylamine.



nitrite (3—4 g.) gradually added, the temperature being kept below 5°. The diazo-solution is added carefully to a cooled solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (40 c.c.). After 12 hours, the solid is filtered off, dried, and extracted with hot alcohol (50 c.c.). The extract is poured into 1% aqueous sodium hydroxide (100 c.c.), which dissolves any 2-nitro-1-naphthol present. The precipitate is filtered off, washed, and distilled with superheated steam. The solid (2.5 g.) in the distillate, after two crystallisations from alcohol, forms long, pale yellow needles, m. p. 76° (Found: N, 7.1; Cl, 16.7.  $C_{10}H_6O_2NCl$  requires N, 6.7; Cl, 17.1%). 1-Chloro-2-nitronaphthalene does not depress the melting point of 2-nitro-1-naphthol.

*1-Bromo-2-nitronaphthalene.*—The above procedure was repeated, except that the Sandmeyer reaction was carried out in a cooled mixture of crystallised copper sulphate (5.4 g.), copper bronze (1.4 g.), sodium bromide (15 g.), and water (40 g.). The solid obtained (0.95 g.) crystallised from alcohol in stout, bright yellow needles, m. p. 97° (Found: N, 5.8; Br, 31.5.  $C_{10}H_6O_2NBr$  requires N, 5.55; Br, 31.7%).

*1-Iodo-2-nitronaphthalene.*—The Sandmeyer reagent in this case was potassium iodide (6 g.) in water (50 c.c.). The solid product was treated with sodium bisulphite solution to remove iodine, and crystallised from alcohol in pale yellow plates, m. p. 111° (yield 1.9 g.) (Found: I, 42.7.  $C_{10}H_6O_2NI$  requires I, 42.4%).

*2-Chloro-1-nitronaphthalene.*—1-Nitro-2-naphthylamine (5 g.) was diazotised according to Friedländer and Littner (*Ber.*, 1915, 48, 330), and from the resulting solution 1 g. of 2-chloro-1-nitronaphthalene was obtained.

*2-Nitronaphthalene.*—A mixture of 2-nitro-1-naphthylamine (4.2 g.), alcohol (12 c.c.), and concentrated sulphuric acid (3 c.c.) was cooled to 0°, 3.4 c.c. of aqueous sodium nitrite (50 g. in 100 c.c. of solution) were added during 30 minutes, and the whole was kept in the cold for 4 hours. It was then gradually heated to the boiling point during 5 hours, boiled for 2 hours, poured into cold water (300 c.c.), 20% aqueous sodium hydroxide (20 c.c.) was added, and the mixture was steam-distilled. The pure 2-nitronaphthalene in the distillate solidified in yellow crystals (1.24 g.) with a cinnamon-like odour, m. p. 79° (Found: N, 8.2. Calc., N, 8.1%).

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals used in this investigation.

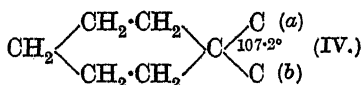
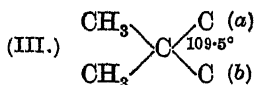
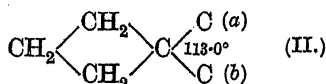
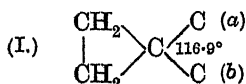
TECHNICAL COLLEGE, HUDDERSFIELD.

[Received, July 25th, 1925.]

III.—*The Influence of Carbon Rings on the Velocity of Reactions involving their Side Chains. Part I. The Hydrolysis of Cyclic and Open-chain Malonic Esters.*

By RICHARD GANE and CHRISTOPHER KELK INGOLD.

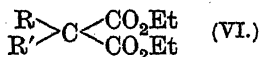
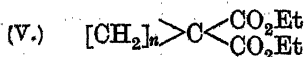
It has been shown during the last 10 years that the angle between two of the valencies of a carbon atom may be materially affected by structural conditions relating to the other two valencies, such as, for instance, their inclusion in a ring (Beesley, Ingold, and Thorpe, J., 1915, 107, 1080, and later papers) or their attachment to groups of larger or smaller molecular volume (Ingold, J., 1921, 119, 305, and later). Thus, on passing through the series (I) to (IV) an increasing



tendency towards the interaction of groups attached to carbon atoms (a) and (b) proves that these two carbon atoms are brought together by the widening of the angle between the remaining two valencies of the central carbon atom.

The opposite sequence would be expected if we were to examine, not the *interaction* of groups attached to carbon atoms (a) and (b), but their *independent* action on some external reagent. Evidently the proximity of the carbon atoms would now be, not an accelerating, but a retarding influence, and a *decreasing* tendency to reaction should be observed on passing through the series (I) to (IV).

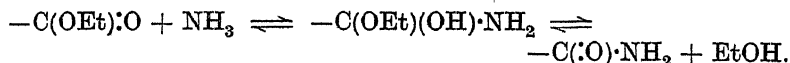
We have been induced to examine this inference, not only for its own interest, but also because the large choice of replacement and addition reactions available renders it possible to select reactions capable of more exact study than the violent ring-forming processes employed in the investigations referred to above. This paper contains a record of experiments on the relative rates of hydrolysis by alkalis of a series of cyclic malonic esters of type (V), certain open-chain malonic esters (type VI) being included for comparison.



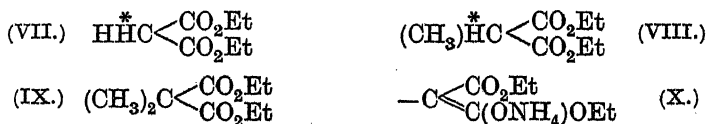
The remarkable effect of different carbon rings in promoting or retarding reactions in which only their side-chains and not the rings themselves are involved was first impressed on us when comparing

the experiences of Fischer and Diltthey (*Ber.*, 1902, **35**, 844) with those of Ingold, Sako, and Thorpe (*J.*, 1922, **121**, 1177) when studying the formation of amides from malonic esters by the aid of aqueous ammonia. This case appears to have special analogies with results recorded in this paper, and must briefly be considered.

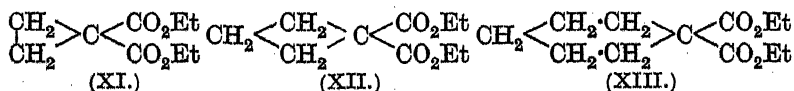
The most rational view of amide formation from esters appears to be that it is the result of two consecutive reversible addition reactions, the first of the aldehyde-ammonia, and the second of the ketone-alcoholate (semi-acetal) type :



Fischer and Diltthey, however, were influenced by the fact that, whilst ethyl malonate and ethyl methylmalonate (VII and VIII) readily yield amides with aqueous ammonia, ethyl dimethylmalonate (IX) refuses to do so, and they therefore formulated the reaction, not as a direct attack by ammonia upon the carbethoxyl groups, but as a complex process involving a tautomeric hydrogen atom (\*), the presence of which in (VII) and (VIII) enables a salt of type (X) to be formed as an intermediate product.



Ingold, Sako, and Thorpe (*loc. cit.*), and at about the same time Dox and Yoder independently (*J. Amer. Chem. Soc.*, 1921, **43**, 2097), prepared without difficulty amides from the cyclic malonic esters (XI) and (XII) which, however, are devoid of a malonyl hydrogen atom.



These observations appear to some extent to rehabilitate the reversible addition mechanism, and to suggest a spatial explanation of the differences noticed. When it is reflected also that amide-formation occurred more easily with the *cyclopropane* than with the *cyclobutane* ester, it seems clear that at least a part of the observed differences is to be accounted for on stereochemical grounds. The special mechanism suggested by Fischer and Diltthey cannot be positively excluded from participation in the cases to which it applies; it must, however, be regarded, not as the general mechanism of amide formation, but only as a possible auxiliary process by means of which amide formation may be facilitated when enolisation of the ester can occur.

Bearing these points in mind, we have examined the velocity of hydrolysis not only of cyclic and disubstituted malonic esters such as (IX), (XI), (XII), and (XIII), but also of a series of malonic esters

FIG. 1.

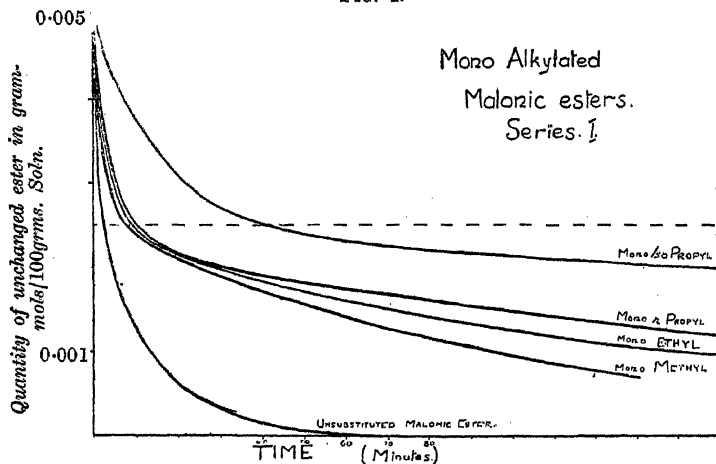
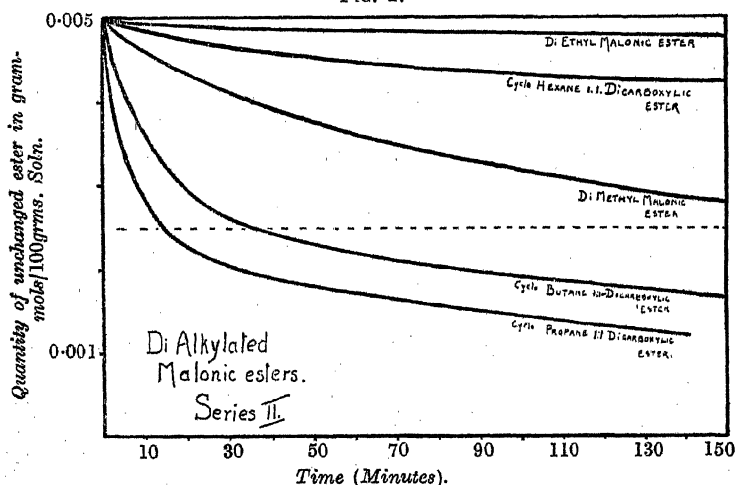


FIG. 2.



possessing a mobile hydrogen atom. The results of some of these determinations, carried out under strictly comparable conditions, are displayed in Figs. 1 and 2.

Attempts to calculate coefficients and construct such curves

theoretically led to considerable mathematical difficulties, principally owing to the distortion which experimental errors underwent in the process of evaluating coefficients. In its simplest aspect, and neglecting all corrections, the complete hydrolysis must be regarded as a pair of consecutive bimolecular reactions, but calculating on this basis it was found that effects of an arbitrary variation of one of the determined coefficients could often be largely counterbalanced by adjusting the other. Finally an approximate numerical comparison of the different cases was obtained by calculating the initial velocities from a series of curves representing identical conditions of temperature and initial concentration.

These initial velocities,  $\dot{x}_0$ , which were calculated from the following equations,

$$\dot{x} = K(a - x)(b - x); K_0 = \lim_{x \rightarrow 0} K; \text{ and } \dot{x}_0 = K_0 ab,$$

are exhibited for the disubstituted malonic esters (cyclic and open-chain) in the following table, the last column of which displays the angle between the valencies carrying the carboxyl groups calculated according to the principles advanced by Beesley, Ingold, and Thorpe (*loc. cit.*).

TABLE I.

	$\dot{x}_0 \times 10^4$ .	$\log_{10} \dot{x}_0$ .	$\theta$ .
<i>cyclo</i> Propane-1 : 1-dicarboxylic ester .....	4.95	4.69	116.9°
<i>cyclo</i> Butane-1 : 1-dicarboxylic ester .....	2.3 (5)	4.37	113.0
<i>gem</i> -Dimethylmalonic ester .....	0.45	5.65	109.5
<i>cyclo</i> Hexane-1 : 1-dicarboxylic ester .....	0.10	5.00	107.2
<i>gem</i> -Diethylmalonic ester .....	0.02 (5)	6.40	(105.3)

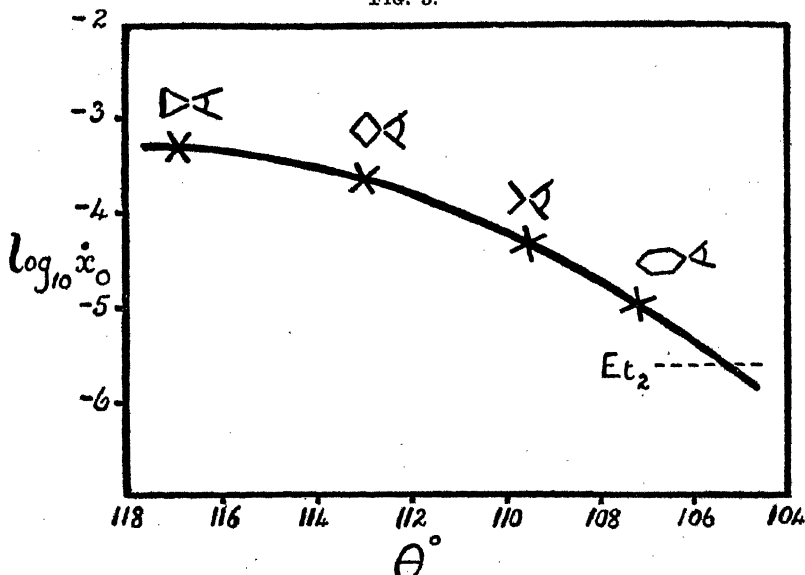
Reference to Fig. 3 shows that the points connecting the logarithms of the initial velocities and the calculated angles lie on a smooth curve both for the cyclic esters and the *gem*-dimethyl ester. There is no means at present of calculating the angle appropriate to the *gem*-diethyl ester, but the curve indicates a value of 105.3°, which is lower than might be expected from previous investigations with glutaric acids.

It was not found possible to deduce initial velocities in the cases of the tautomeric malonic esters represented in Fig. 1, as the reactions of these substances (excepting *isopropylmalonic ester*) were too rapid at their commencement for accurate measurement. The curves show, however, that the various alkyl groups exert an influence appropriate to their relative size, although it is difficult to express this effect quantitatively.

The fact that the reactions of this group proceed with much greater rapidity than the steric theory would indicate seems to show the operation of an additional mechanism when tautomeric hydrogen is present. Such a supposition would be consistent with that

discussed in the case of amide formation, with racemisation by alkalis of compounds containing potentially mobile hydrogen attached to asymmetric carbon, with the interconversion of sugars by alkalis, and numerous other well-known phenomena.

Fig. 3.



## EXPERIMENTAL.

*Preparation of Material.*—(1) *Ethyl malonate*. A sample of Boots's pure ethyl malonate was carefully fractionated, head and tail fractions being rejected, and the main portion, which boiled well within  $1^\circ$ , being used.

(2) *Ethyl methylmalonate*. To avoid possible contamination of the monomethylation product of ethyl malonate with traces of the latter and of ethyl dimethylmalonate, the crude ester was hydrolysed and the acid crystallised several times from ether and water, and, after washing with hot chloroform, from ethyl acetate. The fully purified acid (m. p.  $130^\circ$ ; recorded m. p.  $129^\circ$ ) was then re-esterified by Fischer and Speier's method. The ester had b. p.  $196\text{--}197^\circ/754$  mm.

(3) *Ethyl dimethylmalonate*. The crude dimethylation product of malonic ester was distilled (b. p.  $193\text{--}195^\circ$ ) and, in view of possible contamination with incompletely methylated products, digested with an equal weight of ammonia ( $d$  0.880), which rapidly converts the latter into amides. The pure dimethyl ester had b. p.  $194\text{--}194.3^\circ/751$  mm. and b. p.  $196\text{--}197^\circ/765$  mm.

- (4) *Ethyl ethylmalonate*. Like (2).
- (5) *Ethyl diethylmalonate*. Boots's sample of this ester was shaken with cold 30% sodium hydroxide sufficiently to hydrolyse any ethyl monoethylmalonate, recovered, and distilled (Michael, *J. pr. Chem.*, 1905, 72, 537).
- (6) *Ethyl n-propylmalonate*. The ester prepared as described by Conrad (*Annalen*, 1880, 204, 124) was purified by distillation until it boiled within 1°.
- (7) *Ethyl isopropylmalonate*. Like (6) (compare Preiswerck, *Helv. Chim. Acta*, 1923, 6, 192).
- (8) *Ethyl cyclopropane-1 : 1-dicarboxylate* (XI) was prepared and purified as described by Perkin (*J.*, 1885, 47, 810). B. p. 210—211°/718·5 mm.
- (9) *Ethyl cyclobutane-1 : 1-dicarboxylate* (XII), prepared as described by Perkin (*J.*, 1887, 51, 2) and purified by repeated fractional distillations, had b. p. 224·5—225·5°/757·7 mm.
- (10) *Ethyl cyclohexane-1 : 1-dicarboxylate* (XIII). The specimen used was kindly given by Mr. W. A. Wightman. It had been subjected to partial hydrolysis, which would have removed any monosubstituted malonic ester if present [see (5)].

*Method of Experiment.*—The hydrolyses were carried out by means of carbonate-free aqueous-alcoholic sodium hydroxide contained in strong bottles, into which thin glass tubes containing the weighed ester (usually 0·005 g.-mol.) were dropped to start the reaction, the alkali having previously attained the thermostat temperature. The portions withdrawn for analysis were run as rapidly as possible into an excess of hydrochloric acid to terminate the reaction and titrated with *N*/50—*N*/60-barium hydroxide. Various temperatures and concentrations of alkali were employed, but in the experiments selected for this record the temperature was uniformly 27·0°, whilst the alkali consisted of 0·8380 g. of sodium hydroxide, 23·26 g. of water and 75·90 g. of alcohol in each case.

*Results.*—The general method of calculating the limiting velocities has been described above, and an instance may here be given of its application. In the following table, the figures of the first row are read from the slope of the smoothed  $x-t$  curve, and those in the bottom row show the asymptotic approach of  $k$  to the value  $k_0 = 0·0000090$ ; whence  $\dot{x}_0 = 0·00049$  can be calculated.

TABLE II.

(Ethyl cyclopropane-1 : 1-dicarboxylate.)

$\dot{x} \times 10^4 \dots$	4·45	3·55	2·95	2·40	1·70	1·30	0·78
$x \times 10^4 \dots$	2·25	6·20	9·50	1·21	1·62	1·92	2·24
$k \times 10^4 \dots$	9·2	9·1	9·5	9·6	10·4	12·4	17·4 (rapidly increasing)

TABLE III.  
(Mobile Esters.)

Ethyl malonate.		Ethyl methylmalonate.		Ethyl ethylmalonate.	
<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).
0.50	16.2	0.75	8.5	1.00	6.3
1.50	22.5	3.00	17.8	2.00	11.1
2.50	27.4	4.00	20.7	3.25	15.3
3.75	29.6	6.00	23.1	6.00	20.8
5.75	32.7	8.50	24.9	8.25	24.0
6.75	34.1	11.00	26.2	10.75	25.7
9.75	37.3	15.25	27.4	14.25	26.9
12.00	39.2	20.00	28.5	21.00	28.1
14.75	40.9	25.00	30.0	33.00	30.1
19.50	43.3	30.00	31.1	41.75	31.4
26.50	45.8	35.50	32.3	54.00	32.8
35.50	47.3	46.50	34.3	71.25	34.6
46.00	48.8	60.50	36.5	89.00	35.9
59.00	49.6	75.25	38.1	104.00	37.4
75.0	49.9	89.00	39.3	127.00	39.0
		100.00	40.7	144.00	39.9
		117.00	41.8	165.00	41.2
		131.00	43.0	194.00	42.2

Ethyl <i>n</i> -propylmalonate.				Ethyl isopropylmalonate.			
<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).
0.50	5.7	28.50	33.3	0.50	2.3	41.00	24.7
1.44	10.6	38.75	34.0	2.25	5.8	57.50	26.7
2.50	14.6	70.50	34.7	4.25	7.8	75.25	27.7
4.33	16.4	105.50	36.8	8.50	11.1	91.75	28.5
6.67	22.3	132.50	38.7	14.25	16.0	113.50	28.9
9.44	24.7	153.00	39.4	19.25	18.7	134.50	29.6
12.50	26.6	187.50	40.8	25.00	21.6	174.75	30.4
15.84	29.8	210.25	41.6	35.25	23.8		
20.00	31.2						

TABLE IV.  
(Static Esters—Open-chain.)

Ethyl dimethylmalonate ("A").				Ethyl dimethylmalonate ("B").				Ethyl diethylmalonate.	
<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).	<i>t</i> (mins.).	$x \times 10^4$ (g.-mols.).
0.75	0.3	84.50	16.4	1.50	0.7	85.00	16.9	1.50	0
1.50	0.6	102.25	17.9	3.75	1.3	102.75	17.8	13.00	0.3
3.00	1.3	116.50	19.2	6.25	2.1	121.50	19.3	22.50	0.6
6.84	2.4	138.00	20.6	10.00	3.4	148.50	21.2	34.50	0.9
14.84	4.9	158.75	22.1	17.00	5.6	174.67	22.4	48.25	1.1
26.00	7.4	183.75	23.1	25.75	7.5	201.00	23.5	110.00	1.5
36.75	9.8	200.50	23.8	33.50	8.5	223.00	23.9	181.00	2.2
46.50	11.3	212.25	23.9	41.75	10.6	244.00	24.8	218.00	2.4
56.84	12.9	229.50	24.6	52.75	11.7	278.50	25.0		
70.50	14.8	238.75	24.9	68.25	14.5	309.75	26.5		
				81.75	16.5				



TABLE V.  
(Static Esters—Cyclic.)

Ethyl cyclopropanedicarboxylate.				Ethyl cyclobutanedicarboxylate.				Ethyl cyclohexane- dicarboxylate.	
$x \times 10^4$		$x \times 10^4$		$x \times 10^4$		$x \times 10^4$		$x \times 10^4$	
<i>t</i> (mins.).	<i>t</i> (g.- mols.).	<i>t</i> (mins.).	<i>t</i> (g.- mols.).	<i>t</i> (mins.).	<i>t</i> (g.- mols.).	<i>t</i> (mins.).	<i>t</i> (g.- mols.).	<i>t</i> (mins.).	<i>t</i> (g.- mols.).
0.50	2.8	29.50	29.5	0.50	1.0	44.00	26.3	3.75	0.5
1.75	6.9	34.25	29.9	1.75	3.3	51.00	27.4	7.00	0.8
2.75	10.4	39.00	30.4	3.75	7.2	62.75	28.3	14.00	1.5
4.00	13.1	47.75	31.4	6.50	10.9	78.50	29.8	29.50	2.8
5.50	17.3	56.00	32.6	9.00	13.5	103.50	31.6	49.50	3.9
8.25	19.9	68.50	33.7	14.00	17.0	128.50	32.8	61.00	4.8
11.50	22.6	84.50	35.1	19.33	19.5	147.75	33.2		
14.00	24.6	96.00	35.5	25.33	21.6	170.00	34.4		
17.00	25.7	113.50	36.5	30.00	23.8	188.25	34.9		
20.25	26.9	134.25	37.8	35.20	24.6	207.00	36.1		
24.00	28.3	160.75	38.2						

We desire to thank the Chemical Society for a grant which has covered much of the cost of this investigation.

THE UNIVERSITY, LEEDS.

[Received, November 18th, 1925.]

#### IV.—Tesla-luminescence Spectra. Part VI. Some Amino-derivatives.

By WILLIAM HAMILTON McVICKER, JOSEPH KENNETH MARSH,  
and ALFRED WALTER STEWART.

IN previous papers (J., 1923, 123, 642, 817, 2147; 1924, 125, 1743; 1925, 127, 999) accounts were given of the Tesla-luminescence spectra of various benzene derivatives. The present communication contains a description of the emission spectra of some aromatic amino-derivatives. The apparatus used is the same as before, the pressures were 1—2 mm., and the exposure was in each case 15 minutes.

*Aniline*, b. p. 182.9°/748 mm. A strong continuous spectrum, 2880—4000 Å.U., fading off gradually at both ends, with a number of well-defined narrow bands at 2895, 2915, 2927, 2938, 2960, 2976, 2985, 2999, 3010, 3022, 3031, 3050, 3070, 3098, 3122, 3145, 3171, 3199, 3224.

The spectra of the next seven substances faded gradually at both ends, but more so at the end of greater wave-length.

*Monomethylaniline*, b. p. 196.4—196.9°/770 mm. A strong continuous spectrum at approximately 2965—4250 Å.U. The centre of maximum intensity is about 3300 Å.U.

*Monoethylaniline*, b. p. 205.6—206.2°/770 mm. A strong continuous spectrum at approximately 2695—4250 Å.U. The centre of maximum intensity is about 3340 Å.U.

*Dimethylaniline*, b. p. 194.2—194.3°/766 mm. A strong continuous spectrum at approximately 3025—4300 Å.U. Centre of maximum intensity at approximately 3420 Å.U.

*Diethylaniline*, b. p. 213.2—214°/738 mm. Medium continuous spectrum at approximately 3010—4225 Å.U. Centre of maximum intensity at approximately 3375 Å.U.

*isoAmylaniline*, b. p. 253.6—255.6°/766 mm.† Strong continuous spectrum at approximately 2995—4300 Å.U. Centre of maximum intensity at about 3340 Å.U.

*Benzylamine*, b. p. 184.6—185.2°/771 mm. Weak continuous spectrum at approximately 2671—3390 Å.U. Diffuse heads of bands at 2671, 2714, 2800.

*Benzylaniline*, b. p. 320.8—321.0°/775 mm. Strong continuous spectrum at approximately 2980—4225 Å.U. Centre of maximum intensity at approximately 3345 Å.U.

*Diphenylamine*, b. p. 302.6—302.8°/750 mm. Weak continuous spectrum at approximately 3070—3875 Å.U., fading off gradually at both ends.

*Triphenylamine*. Nine times recrystallised from alcohol and boiled once with animal charcoal. M. p. 126.4°. Moderate continuous spectrum at approximately 3260—4220 Å.U., fading off gradually at both ends.

*Benzidine*, m. p. 125—127°. Strong continuous spectrum at about 3200—4600 Å.U., fading off gradually at both ends but more so at the end of shorter wave-length. Centre of maximum emission at approximately 3830 Å.U.

*Hydrazobenzene*, m. p. 126—127°. Very faint, continuous spectrum at approximately 3050—4125 Å.U., fading off gradually at both ends, but more so at end of greater wave-length. Centre of maximum intensity at approximately 3340 Å.U.

*Phenylhydrazine*, b. p. 241.0—241.5°/763 mm. Weak continuous spectrum at approximately 2980—3640 Å.U., fading off gradually at both ends. Possibly there are faint narrow bands at 3024 and 3052 Å.U.

*α-Methylphenylhydrazine*, b. p. 101—103°/28—29 mm. Strong continuous spectrum at approximately 2940—4225 Å.U., fading off gradually at both ends, but more so at the end of greater wave-length. Centre of maximum intensity at approximately 3345 Å.U.

*α-Naphthylamine*, b. p. 299.4—299.7°/774 mm. Intense continuous spectrum at approximately 3320—4700 Å.U., fading off gradually at both ends with a diffuse head at about 3780 Å.U.

Signs of very indistinct bands were observed at approximately 3340, 3399, 3443, and 3506 Å.U., but the phenomena are doubtful.

*β-Naphthylamine*, m. p. 110°. Intense continuous spectrum at approximately 3280—4700 Å.U., fading off gradually at both ends. Centre of maximum intensity at approximately 3800 Å.U.

*Ammonia*. The ammonia spectrum contains two maxima at 3360 and 3371 Å.U. and a band system extending from these in both directions to 3286 and 3450, respectively. Possibly there may be two bands in the visible region at 5690 and 6600 Å.U. These bands are very indefinite. The spectrum in general is that of ammonia in a vacuum tube excited by an ordinary induction coil discharge.

On collating the foregoing data, some points of interest are found. The attachment of the amino-group directly to the benzene ring has the effect of shifting the region of emission towards the red end. Replacement of the hydrogen atoms of the amino-group by alkyl radicals has no profound influence on the spectral character of the emission. When phenyl groups are introduced into the amino-radical, the first phenyl group weakens the intensity of the spectrum as a whole, whilst a second phenyl radical increases the intensity slightly, though not enough to bring it back to the intensity of aniline.

The replacement of one hydrogen atom of the amino-group by the group  $-\text{NH}_2$  so as to form phenylhydrazine, has a marked influence on the spectrum. Aniline has a strong emission with a length of 1120 units; the emission of phenylhydrazine is weak and extends over only 660 units. If the imino-group of phenylhydrazine carries a methyl group,  $\text{NMePh}\cdot\text{NH}_2$ , both the intensity and the extent of the emission are increased. On the other hand, the introduction of a phenyl group, forming  $\text{NHPh}\cdot\text{NHPh}$ , weakens the intensity of the spectrum but increases the extent of the emission.

The influence of constitution upon the spectra is seen by comparing the following data :

		Intensity.	Emission region.
Diphenylmethane	$\text{CH}_2\text{Ph}_2$	Medium	2673—3900
Diphenylamine	$\text{NHPh}_2$	Weak	3070—3875
Dibenzyl	$\text{CH}_2\text{Ph}\cdot\text{CH}_2\text{Ph}$	Faint	2700—4300
Hydrazobenzene	$\text{NHPh}\cdot\text{NHPh}$	Very faint	3050—4125
Benzidine	$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$	Strong	3200—4600
Diphenyl	$\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5$	Faint	2890—3900

Obviously when imino-groups are substituted for methylene groups the intensity is weakened and the spectrum is truncated at the violet end. Hydrazobenzene has a very faint spectrum, whereas the spectrum of benzidine is strong. The intensity of the benzidine spectrum is not due to the close proximity of the two

phenyl nuclei, since the parent substance, diphenyl, has only a faint spectrum. The difference in the spectra of the two isomeric compounds must therefore be sought in difference between the group  $-\text{NH}-\text{NH}-$  on the one hand and the two primary amino-groups on the other.

The introduction of an amino-group into naphthalene has the effect of shortening the original spectrum at both ends while making it more intense in the region in which it still persists.

We desire to express our indebtedness to the Research Fund Committee of the Society; and also to the Eastman Kodak Company, who supplied us with specially pure specimens of some of our materials.

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[Received, October 7th, 1925.]

### V.—*The Solubility of Sodium Iodide in Ethyl Alcohol.*

By FREDERICK ERNEST KING and JAMES RIDDICK PARTINGTON.

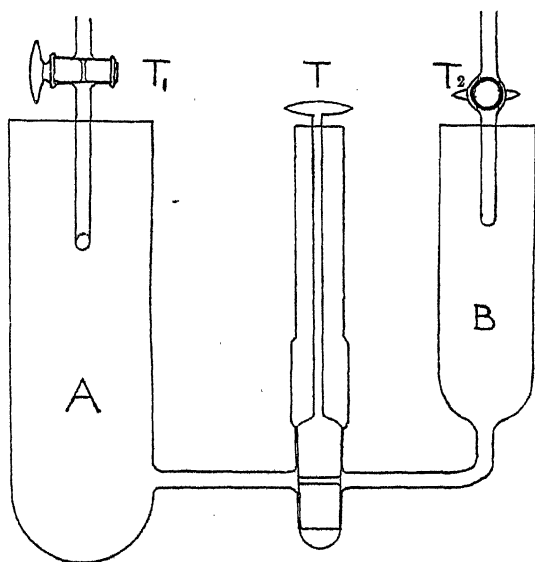
THE solubilities of the iodides of the alkali metals in alcohol require reinvestigation on account of the probable presence of moisture in the materials previously employed.

*Preparation of the Materials.*—*Ethyl alcohol.* Two litres of 96% alcohol were poured on to freshly burnt quicklime, refluxed for 6 hours, distilled, and refluxed over a further quantity of lime. The alcohol was distilled on to 5 g. of powdered silver nitrate previously dried at  $110^{\circ}$ , refluxed, and distilled. The distillate was refluxed with about 20 g. of fresh calcium turnings and distilled through a tall column, the first and last fractions of 100 c.c. being rejected. The alcohol was stored in a vessel with a siphon attachment and a guard tube of phosphorus pentoxide. The alcohol was free from aldehyde, ketone, ethyl nitrite, and ammonia. The density ( $D_{20}^{20}$ ) was 0.7851.

*Sodium iodide.* The iodide was prepared by decomposing pure sodium carbonate with hydriodic acid of constant b. p. ( $126^{\circ}$ ), prepared by the action of hydrogen sulphide on iodine in the presence of water. The solution of sodium iodide, slightly coloured with iodine from the decomposition of a little of the acid by the air, was evaporated to dryness and the solid recrystallised three times from water. The crystals of  $\text{NaI} \cdot 2\text{H}_2\text{O}$  were heated in a large porcelain boat in a sloping glass tube through which a slow current of pure dry hydrogen was passing. The electrolytic hydrogen used in these

experiments was contained in a cylinder and was freed from oxygen by passing over heated platinised asbestos. As the water was driven off from the iodide the temperature was increased to  $120^{\circ}$ . The white solid was cooled in dry hydrogen, removed quickly, and ground up in a mortar contained in a desiccator over phosphorus pentoxide (Parker, J., 1914, 105, 1504). Spectrum analysis failed to reveal the presence of other metals and the iodine content was shown to be 84.64% by precipitation as silver iodide (Theory, 84.66%).

FIG. 1.



*Experimental.*—On account of the hygroscopic nature of the solution the apparatus shown in Fig. 1 was devised. The apparatus was carefully dried and an excess of sodium iodide, together with the alcohol, placed in the tube A. The tube was closed with a good cork, which had been dried by heating in a wax-bath at  $120^{\circ}$ , and fitted with a glass stirrer. The air in the tube was displaced by dry hydrogen through the tap,  $T_1$ , and the vessel was then closed by pouring mercury into the seal surrounding the stirrer. Tube B was closed with a rubber bung, through which passed a filter tube packed with dry cotton wool, reaching to the bottom of B, with the top ground to take the end of a standard pipette. The capacity of A was approximately 80 c.c. and that of B 30 c.c. Tube B was filled with dry hydrogen and closed at the top of the filter tube with pressure tubing and a clip. Connexion between A and B could be made through the enclosed tap, T.

The apparatus was placed in a thermostat maintained at  $25.0^{\circ}$ , and the alcohol and iodide were stirred over-night. The stirring was then discontinued, and a sample of the saturated solution of iodide transferred to B through T by suction through  $T_2$ , dry hydrogen being admitted through  $T_1$  to take the place of the solution removed. Quantities of approximately 10 c.c. of the solution were removed in standard pipettes and rapidly transferred to weighed evaporating flasks fitted with ground glass stoppers having two tubes sealed into them, the outer ends being provided with ground glass caps. The weights of the solutions were found, the solutions evaporated to dryness, the residues heated to  $120^{\circ}$  in a stream of dry hydrogen, and weighed. The solubility of sodium iodide in alcohol at  $25^{\circ}$  was found and an approximate value for the density of the solution as compared with water as a standard was calculated.

*Results.*—The figures under  $S^{25}$  represent the solubilities of sodium iodide in ethyl alcohol at  $25^{\circ}$  in g. per 100 g. of alcohol.

Expt. ...	1	2	3	4	5	6	7	8	9	10
$S^{25}$ .....	42.82	42.39	42.20	42.13	42.89	42.83	42.84	42.24	42.50	42.89

Density ( $D^{25}$ ) = 1.037. Mean value of  $S^{25}$  = 42.57.

Pure dry lithium iodide has been prepared by heating the monohydrate in a current of dry nitrogen free from oxygen, and investigations on the influence of the solubility of lithium iodide on the solubility of sodium iodide in alcohol are in progress.

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[Received, November 13th, 1925.]

## VI.—The Structure of the Normal Monosaccharides. Part III. Rhamnose.

BY EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH.

As earlier work led to the conclusion that normal derivatives of the pentose sugars xylose and arabinose have the amylene-oxidic structure (Hirst and Purves, J., 1923, **123**, 1352; Hirst and Robertson, J., 1925, **127**, 358), it was obviously of interest to determine the structure of normal derivatives of a typical methyl pentose. Evidence is now submitted showing that *l*-rhamnose and its stable derivatives also are amylene-oxidic. This view conflicts with the suggestion of Pringsheim ("Zuckerchemie," 1925, p. 102) that a butylene-oxidic structure for rhamnose follows from the apparently definite furoidal structure of rhamnal (Bergmann and Schotte, *Ber.*, 1921, **54**, 404). Fischer, Bergmann, and Rabe (*Ber.*, 1920, **53**, 2362) found, however, that during the conversion of aceto-

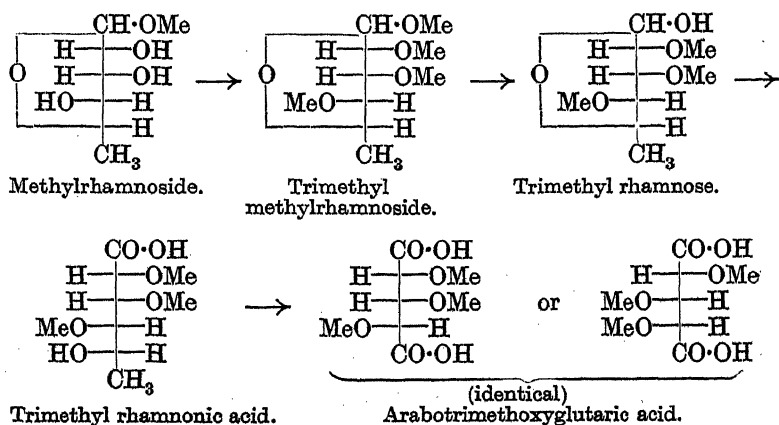
bromorhamnose into triacetyl methylrhamnoside a mixture of isomeric substances is formed by the wandering of acetyl groups accompanied by corresponding changes in the nature of the oxidic linkings. We are therefore of the opinion that it would be unsafe to base the structure of rhamnose derivatives on that of rhamnal, and, when considered in the light of the work now described, the presence of a  $\gamma$ -oxidic linking in triacetyl rhamnal is to be taken rather as evidence of the occurrence of an isomeric change during the reduction of acetobromorhamnose than as proof of the constitution of rhamnose itself.

The observations of Fischer, Bergmann, and Rabe led us to consider with special care the stability of the methoxyl groups in methylated rhamnose, for any wandering of the methyl groups would complicate very seriously the oxidation method we proposed to use in determining the structure of the compound. A wandering of a methyl group from position 6 to position 3 in the glucose molecule has been suggested (Ohle, *Ber.*, 1924, 57, 403) to explain certain discordant observations in the chemistry of the acetone derivatives of the sugars, but, so far as we are aware, no case of such a transformation has been encountered during the oxidation of a methylated carbohydrate. Both  $\gamma$ - and normal derivatives oxidise to stable methoxy-acids without wandering of the methyl groups (compare, *e.g.*, Irvine, Fyfe, and Hogg, *J.*, 1915, 107, 539; Irvine and Oldham, *J.*, 1921, 119, 1744; Pryde, *J.*, 1923, 123, 1808; Levene, *J. Biol. Chem.*, 1924, 60, 167; Haworth and Baker, *J.*, 1925, 127, 365; etc.). A study of methylated rhamnose and its oxidation has convinced us that the course of oxidation is normal in this case also, and that in consequence the structure of methylated rhamnose may be deduced when the nature of the oxidation products is known.

Rhamnose indeed, when methylated under various conditions, has shown a rather unusual capacity for yielding methyl derivatives of one structural form only. On methylation, either by preliminary formation of the crude mixture of  $\alpha$ - and  $\beta$ -methylrhamnosides with acid methyl alcohol followed by use of the Purdie reagents, or by direct treatment with methyl sulphate, only the normal trimethyl rhamnose (Purdie and Young, *J.*, 1906, 89, 1194) was obtained, whereas in many cases mixtures containing both the amylen- and the butylene-oxide form of the methylated sugar are produced (Pryde, Hirst, and Humphreys, *J.*, 1925, 127, 348).

Oxidation of this trimethyl rhamnose by nitric acid not only showed that the compound was free from admixture with isomeric forms of different oxidic linking, but also gave a direct proof of its constitution. The oxidation product under the special conditions

adopted was *l*-arabotrimethoxyglutaric acid, which may also be obtained by oxidising trimethyl arabinose or by methylating *l*-trihydroxyglutaric acid. No methoxy-group was lost during the reaction, but the terminal methyl group was removed. These observations can be interpreted (assuming the stability of the methoxy-groups) only on the basis of an amylenic-oxidic structure for normal trimethyl rhamnose, and from arguments which have been detailed previously this leads to the assigning of the amylenic-oxidic formula to  $\alpha$ - and  $\beta$ -methylrhamnosides and in all probability to rhamnose itself. A summary of the reactions involved is given in the accompanying scheme.



The mechanism of the oxidation is in itself interesting. After the production of the intermediate trimethylrhammonic acid, the action of nitric acid on the terminal  $-\text{CH}(\text{OH})\cdot\text{CH}_3$  group involves a quantitative transformation to  $-\text{CO}\cdot\text{OH}$  and  $\text{CO}_2$ . This must proceed *via* the ketone  $-\text{CO}\cdot\text{CH}_3$ , and the present reaction (although not in accord with the usual behaviour of methyl ketones) is thus brought into line with certain other instances. For example, lævulic acid yields succinic acid on treatment with nitric acid (Tollens, *Annalen*, 1881, 206, 257) and rhamnose itself gives *l*-trihydroxyglutaric acid (Will and Peters, *Ber.*, 1889, 22, 1697). The simple nature of the change is here emphasised because of its contrast with the more complicated course of oxidation undergone by the allied group  $-\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OMe}$ .

A study of the latter question has been completed by one of us in connexion with work on glucose, and details of this will be given in a future communication.



## EXPERIMENTAL.

*Methylation of Rhamnose.*—A mixture of  $\alpha$ - and  $\beta$ -methylrhamnosides (Fischer, *Ber.*, 1895, 28, 1158) was methylated in the manner described by Purdie and Young (*loc. cit.*). The trimethyl  $\alpha$ -methylrhamnoside so prepared showed the properties and physical constants given by these authors (b. p.  $101^{\circ}/9$  mm.;  $[\alpha]_D - 15^{\circ}$  in water;  $[\alpha]_D - 54^{\circ}$  for  $c = 2.15$  in alcohol. The refractive index, hitherto unrecorded, was  $n_D^{15} = 1.4415$ ).

In a second series of experiments rhamnose was treated in the usual way with methyl sulphate and caustic soda. Two such treatments followed by one with silver oxide and methyl iodide gave in good yield the fully methylated sugar as a colourless, uncrystallisable syrup, b. p.  $100-101^{\circ}/9$  mm.,  $n_D^{15} 1.4415$  (Found: C, 54.5; H, 9.2; OMe, 55.2. Calc., C, 54.5; H, 9.1; OMe, 56.3%). It was stable to alkaline potassium permanganate solution and showed  $[\alpha]_D - 11.3^{\circ}$  in alcohol ( $c = 1.77$ ) and  $+ 11.5^{\circ}$  in water ( $c = 2.002$ ). It was therefore a mixture of the  $\alpha$ - and  $\beta$ -forms of trimethyl methylrhamnoside. On hydrolysis with 8% aqueous hydrochloric acid at  $90^{\circ}$ , the specific rotation decreased regularly from the initial value of  $+ 15.5^{\circ}$  ( $c = 1.159$ ) to zero after 40 minutes and then rose gradually to a constant value,  $+ 21.2^{\circ}$  ( $c = 1.085$  as trimethyl rhamnose), after 200 minutes. On plotting the values against time, a curve is obtained which is characteristic of the hydrolysis of a mixture of the  $\alpha$ - and  $\beta$ -forms of a methyl aldside. Experiments on a larger scale gave a final value of  $+ 19.5^{\circ}$  ( $c = 6.4$ ) (compare Purdie and Young, *loc. cit.*). An improved method was employed to isolate the trimethyl rhamnose. After neutralisation of the acid with barium carbonate the hydrolysis product was extracted with chloroform and purified by distillation (yield 75%), being thus obtained as a colourless, viscous syrup, b. p.  $141^{\circ}/19$  mm. (bath at  $153^{\circ}$ ),  $n_D^{15} 1.4565$  (Found: C, 52.3; H, 8.7; OMe, 44.7. Calc., C, 52.4; H, 8.7; OMe, 45.1%).  $[\alpha]_D + 24.9^{\circ}$  (in water,  $c = 2.53$ ),  $- 9^{\circ}$  (in alcohol,  $c = 1.36$ ). It was obviously identical with the trimethyl rhamnose prepared by Purdie and Young.

*Oxidation of Trimethyl Rhamnose.*—A solution of 3.0 g. of trimethyl  $\alpha$ -methylrhamnoside (prepared from  $\alpha$ -methylrhamnoside; or trimethyl rhamnose may be used) in 70 c.c. of nitric acid ( $d 1.2$ ) was heated slowly until oxidation commenced, at  $85^{\circ}$ . The reaction proceeded vigorously and was apparently complete after 4 hours. Heating was then renewed, and continued for a further  $2\frac{1}{2}$  hours. The oxidation product was freed from nitric acid, dried, and esterified with acid methyl alcohol by the method described in previous papers of this series. The ester (2.61 g. or 77% of the

theoretical yield) was purified by distillation and thus obtained as a colourless, uncrystallisable syrup [2.41 g.; b. p.  $135^{\circ}/9$  mm. (bath at  $150^{\circ}$ );  $n_D^{20}$  1.4350;  $[\alpha]_D + 47.6^{\circ}$  (in methyl alcohol,  $c = 1.706$ )]. It behaved as an ester on titration, and analysis and a comparison of its physical constants with those of an authentic sample prepared from arabinose showed it to be dimethyl *l*-arabotrimethoxyglutarate ( $n_D^{21}$  1.4355; b. p.  $143^{\circ}/18$  mm.;  $[\alpha]_D + 47.3^{\circ}$  for  $c = 1.842$  in methyl alcohol) [Found: C, 47.8; H, 7.25; OMe, 60.2; CO<sub>2</sub>Me (by hydrolysis), 46.3. Calc., C, 48.0; H, 7.2; OMe, 62.0; CO<sub>2</sub>Me, 47.2%]. In view of the large difference in rotatory power between the acid and its fully methylated dimethyl ester (Hirst and Robertson, *loc. cit.*), it was of interest to examine the rotation of the sodium salt. A weighed quantity of the ester was hydrolysed with just more than the calculated quantity of caustic soda, and the solution was exactly neutralised with hydrochloric acid;  $[\alpha]_D + 25^{\circ}$  was thus found for the sodium salt (compare Purdie and Irvine, J., 1901, 79, 962, for the rotations of dimethyl *d*-dimethoxysuccinate and the corresponding sodium salt).

When the ester was treated with methyl alcohol saturated with dry ammonia (0.36 g. in 3.6 c.c.), crystals of the diamide separated after 15 hours, and after 3 days 0.20 g. was collected (63% yield). The crystals were washed with cold methyl alcohol and ether and recrystallised once from methyl alcohol; they then had m. p.  $230^{\circ}$ , alone or mixed with an authentic specimen of *l*-arabotrimethoxyglutardiamide. The solubilities, the crystalline form, the behaviour on heating, and the specific rotation of this substance were in exact agreement with those previously recorded.  $[\alpha]_D + 50.4^{\circ}$  ( $c = 0.6942$  in water) (Found: OMe, 41.6. Calc., OMe, 42.3%).

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## VII.—*The Specific Heats of Hydrocyanic Acid.* *A Reply.*

By EDITH HILDA INGOLD.

EARLY this year, a paper by Partington and Carroll appeared (*Phil. Mag.*, 1925, 49, 665) dealing with the ratio of the specific heats of hydrocyanic acid. The author's previous measurements of this constant (J., 1922, 121, 1604) were discussed at some length and criticised on two distinct grounds.

The first of these criticisms is summed up in the remark that "the results obtained by Usherwood, although interesting and useful, are approximate only." \* Since results of moderate precision were all that the author attempted to obtain, no exception could be taken to this statement were it not made in association with comments relating to the author's experimental procedure which are without foundation in fact, and are apparently intended to suggest a want of care. Thus, Partington and Carroll state: "The gas used, obtained by the action of dilute sulphuric acid on potassium cyanide,† scarcely fulfils the purity requirements required for the determination of physical constants." It was, however, made clear in the original experimental description (*loc. cit.*, p. 1609), and may again be emphasised, that the "gas used" was not, as this sentence implies, taken *straight from the generating apparatus into the sound-tube*, but was *first liquefied*, dried, fractionated until its boiling point was constant, and frozen, before use. A specimen of hydrocyanic acid, prepared by this method, has recently been sent for the determination of physical constants to another worker, who reports that he has found it satisfactory. Another similar criticism is that the author made no mention of "precautions taken to prevent contamination of the vapour by air, due to leakage into the apparatus." It is true that since the elementary precaution of ensuring that an apparatus is gas-tight is not peculiar to the experiments described, it was omitted from the experimental description. It may now be stated, however, (a) that the apparatus *was* tested for leakage before and after every experiment, (b) that (excepting in preliminary experiments which were not published) no leakage was found, (c) that the arrangement was such that if there had been a leak hydrocyanic acid would have passed into the air, not *vice versa*.

The second main criticism offered by Partington and Carroll is that the results obtained by the author are due not, as was suggested, to the thermal effect accompanying isomeric change, but to the thermal effect accompanying polymerisation, the occurrence of which, in the vapour of hydrocyanic acid, is, according to Partington and Carroll, indicated by the author's measurements of its density.

\* This conclusion is not, as might perhaps be thought, based on any obvious disagreement between the author's results and those of Partington and Carroll; nor do these authors claim that their measurements are of superior precision, although they may well be, having evidently been conducted with great care and attention to detail. They were carried out at the ordinary temperature and under reduced pressures, whereas the author's observations were made at elevated temperatures.

† It was actually pure sodium cyanide, as appears from the description given (*loc. cit.*, p. 1609).

These measurements showed that, although above about  $170^{\circ}$ , the density is normal (ideal) to within the limits of experimental error (estimated as 0.2%), on approaching the point of liquefaction substantially higher densities obtain, the value at the lowest temperature investigated being nearly 4% above the theoretical. This type of behaviour is, of course, well known. Vapour densities about 3—6% higher than the theoretical were observed by S. Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374) for a great variety of substances, including many, such as fluorobenzene, benzene, hexane, pentane, etc., which could not be suspected of any noteworthy tendency to polymerise. The inert gases exhibit the same characteristic. Partington and Carroll, however, regard such density values as indicating in the case of hydrocyanic acid, not deviations from the gas laws, that is, deviations due to molecular attraction and molecular size (the  $a$  and  $b$  of van der Waals), but polymerisation. Thus the observed 4% excess over the theoretical density is interpreted as indicating that approximately 8% of the molecules have combined to form  $(\text{HCN})_2$ . This view of vapour density results appears to the author entirely contrary to accepted principles. If it were valid, the continuity of state would demand that compressed gases and even ordinary liquids (the densities of which at *N.T.P.* may be thousands of times their ideal vapour densities) must consist principally of enormously polymerised molecules; indeed there would be no such thing as a non-associated liquid. In contradistinction to this view, the author wishes to maintain that, since hydrocyanic acid behaves, in regard to vapour density, similarly to numerous other substances, including inert gases and paraffin hydrocarbons, which are non-associated *even in the liquid state*, and can therefore safely be assumed to be non-associated as vapour, the densities observed in the case of hydrocyanic acid vapour near the point of liquefaction are to be interpreted, not as proving association, but as effects due to departure from the condition (point-molecules without attraction) imagined in an ideal gas. Partington and Carroll refer to the "association" of water vapour as an established fact, and certainly, since liquid water is markedly associated, its vapour would be expected to afford a particularly favourable case for the detection of association in the gaseous state. Yet Kendall (*J. Amer. Chem. Soc.*, 1920, **42**, 2477; compare Menzies, *ibid.*, 1921, **43**, 851) has proved conclusively that, despite its enhanced density, the degree of association of water vapour, if not zero, is at any rate so small that the most accurate available measurements fail to show it. Numerous other cases in which density results had previously been interpreted as indicating association in the vapour have been shown by Kendall and Menzies

to be completely accounted for by deviations from the gas laws.\*

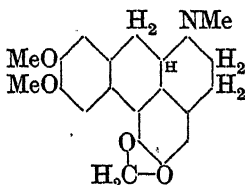
THE UNIVERSITY, LEEDS.

[Received, November 5th, 1925.]

### VIII.—Resolution of *dl*-Dicentrine.

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun.,  
and JOHN RANKIN.

IN a previous communication (J., 1925, 127, 2018), the synthesis of a *dl*-base,  $C_{20}H_{21}O_4N$ , having the constitution



suggested by Gadamer (*Arch. Pharm.*, 1911, 249, 701) for dicentrine is described and it was pointed out that the synthetical base exhibits a series of colour reactions identical with those described by Asahina (*Arch. Pharm.*, 1909, 247, 206) as characteristic of naturally occurring *d*-dicentrine. It has now been found that the *dl*-base may be readily resolved into its *d*- and *l*-modifications by means of tartaric acid under conditions similar to those employed by Gadamer (*loc. cit.*, p. 688) for the resolution of *dl*-glaucine. The *d*- and *l*-modifications crystallise well from ether, melt at 169°, and have  $[\alpha]_D + 64.1^\circ$  and  $- 63.5^\circ$ , respectively.

\* Partington and Carroll calculate that at the critical point hydrocyanic acid must "consist almost entirely of double molecules." On similar principles, argon at the critical point should mainly consist of  $A_3$ . On the other hand, the possibility of association near the critical point (*i.e.*, under high pressure) must be admitted in the case of substances which are associated as liquids, and hence critical data must be used with caution in such cases.

Partington and Carroll's remaining criticisms relate principally to the author's method of calculating the results. For instance, they propose correcting for the variation with temperature of the specific heats of air; a correction which was omitted, since it makes a difference of only about 3 units in the fourth significant figure. They also suggest an alternative method (based on "calculated" critical data) for correcting for deviations from the gas laws, but later in their paper declare it to be unjustified for the reason given above. Bredig and Teichmann (*Z. Elektrochem.*, 1925, 31, 449) observed critical data in fairly good agreement with those used by Partington and Carroll, but near the critical point a curved "rectilinear diameter" was obtained, which may indicate appreciable association under these conditions (Guye, *Arch. Sci. phys. nat.*, 1894, 31, 38).

These constants agree closely with those assigned to dicentrine by Asahina (*loc. cit.*; m. p. 168—169°;  $[\alpha]_D + 62.7^\circ$ ) and a direct comparison of the *d*-base with a specimen of *d*-dicentrine which Professor Gadamer kindly sent us definitely established identity.

#### EXPERIMENTAL.

*dl*-Dicentrine was prepared in the way described in our earlier communication (*loc. cit.*). Commencing with 30 g. of homoveratrylhomopiperonylamine, 7.5 g. of the dihydrochloride of 6'-aminoveratrylhydrohydrastinine were obtained and this yielded 1.3 g. of pure *dl*-dicentrine, m. p. 181° (corr.).

In an attempt to devise an alternative method for the preparation of 6'-nitroveratrylhydrohydrastinine, 6'-nitroveratrylnorhydrohydrastinine (1.5 g.), water (7 c.c.), 40% formalin (0.5 c.c.), and anhydrous formic acid (0.8 c.c.) were heated for 6 hours at 160—170° in a sealed tube. The contents of the tube were diluted with water, and the pale yellow needles collected and recrystallised from alcohol (m. p. 119°) and identified as 6-nitrohomoveratrole. The acid solution was made alkaline with sodium hydroxide, allowed to remain for 24 hours, the precipitate collected, washed with water and crystallised from petroleum (b. p. 40—60°), separating in colourless plates, m. p. 56—58° (Found: C, 68.9; H, 6.7. Calc. for  $C_{11}H_{13}O_2N$ , C, 69.1; H, 6.8%). The identity of this substance with hydrohydrastinine was confirmed by the preparation of the methiodide, which crystallised from methyl alcohol in colourless, rhombic prisms, m. p. 229°, and by the fact that on oxidation with iodine a solution was obtained which exhibited the characteristic hydrastinine fluorescence. The formation of 6-nitrohomoveratrole and hydrohydrastinine under the influence of formaldehyde and formic acid involves a reduction, a methylation, and a scission of the molecule of a kind similar to that observed by Hope and Robinson (J., 1911, 99, 2114) when they obtained 2·6-dinitrotoluene and cotarnine by heating anhydrocotarnine-2:6-dinitrotoluene with glacial acetic acid.

*Resolution of dl-Dicentrine.*—A 2*N*-absolute alcoholic solution of *d*-tartaric acid (0.6 c.c.) was added slowly to a solution of *dl*-dicentrine (0.5 g.) in absolute alcohol (25 c.c.) until a faint acid reaction was observed towards litmus. The clear tartrate solution was converted into the hydrogen tartrate by the gradual addition of a further quantity of *d*-tartaric acid (0.6 c.c.); an amorphous precipitate then separated which redissolved on gently warming. On vigorously scratching, *l*-dicentrine hydrogen *d*-tartrate (0.2 g.) separated from the warm solution in small crystals which, after cooling, were collected and washed with alcohol.

The filtrate and washings were evaporated to dryness, the gummy residue dissolved in water, the bases liberated by the addition of sodium hydroxide, extracted with ether, the extract dried, and the ether removed. The residue (0.37 g.) was dissolved in absolute alcohol (20 c.c.) and titrated with a 2*N*-absolute alcoholic solution of *l*-tartaric acid (0.45 c.c.) \* until a faint acid reaction was obtained. The clear solution was then treated with a further quantity of *l*-tartaric acid (0.45 c.c.); an amorphous precipitate then separated which redissolved on gently warming. *d*-Dicentrine hydrogen *l*-tartrate (0.2 g.) separated, on scratching, as a crystalline powder, which was collected and washed with alcohol.

The salts in the filtrate and washings were reconverted into base and the treatment with *d*- and *l*-tartaric acid was repeated under the same conditions, when further quantities of *l*-dicentrine hydrogen *d*-tartrate (0.1 g.) and *d*-dicentrine hydrogen *l*-tartrate (0.1 g.) were obtained.

Both *l*-dicentrine hydrogen *d*-tartrate and *d*-dicentrine hydrogen *l*-tartrate are soluble in water but almost insoluble in alcohol, and both crystallise from alcohol containing a little water in colourless, nodular masses.

*d*-Dicentrine was obtained by dissolving the recrystallised *d*-dicentrine hydrogen *l*-tartrate in water, making slightly alkaline with sodium hydroxide, extracting with ether, drying over anhydrous sodium sulphate, and concentrating the filtered ethereal solution, when *d*-dicentrine separated in long, colourless prisms, m. p. 169° (corr.). When mixed with a specimen of the *d*-dicentrine obtained from Professor Gadamer, no alteration in m. p. was observed. In chloroform solution:  $l = 1$ ,  $c = 1.433$ ;  $\alpha_D^{25} = 0.92^\circ$ , whence  $[\alpha]_D^{25} = +64.1^\circ$ . *d*-Dicentrine is readily soluble in alcohol, ethyl acetate, and benzene, almost insoluble in petroleum, and is more soluble in ether than *dl*-dicentrine. It is readily soluble in chloroform, the solution gradually becoming yellow (compare Asahina, *loc. cit.*). The recovery of the base from the chloroform solutions used for optical measurements is a wasteful process, because when the solutions are concentrated a double compound insoluble in ether separates. This can be decomposed by the addition of a little methyl-alcoholic potassium hydroxide and the *d*-dicentrine crystallised from ether, when it is recovered as prisms (m. p. 169°), which, however, are always yellow.

*l*-Dicentrine was obtained from recrystallised *l*-dicentrine hydrogen *d*-tartrate exactly as described in the case of the *d*-base. It crystallises from ether in long, colourless prisms, m. p. 169°

\* Our thanks are due to Sir W. J. Pope for the *l*-tartaric acid used in these experiments.

(corr.). When mixed in about equal proportions with a specimen of *d*-dicentrine, the mixture softens at  $168^{\circ}$ , but does not melt completely until about  $178^{\circ}$ . In chloroform:  $l = 1$ ,  $c = 1.700$ ,  $\alpha_D^{25} = -1.08^{\circ}$ , whence  $[\alpha]_D^{25} = -63.5^{\circ}$ . *l*-Dicentrine resembles the *d*-base in its behaviour towards solvents and is recovered as yellow prisms, m. p.  $169^{\circ}$ , from a chloroform solution.

One of us (R. D. H.) is indebted to the Commissioners of the 1851 Exhibition for a studentship which has enabled him to take part in this research, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of the investigation

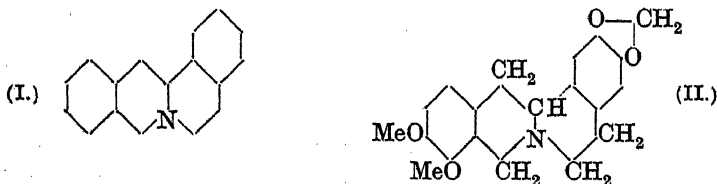
DYSON PERRINS LABORATORY,  
OXFORD.

[Received, November 21st, 1925.]

### IX.—*Synthetical Experiments in the isoQuinoline Group. Part VI. A Synthesis of Derivatives of Paraberine.\**

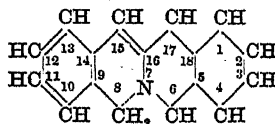
By RAY CAMPBELL, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

THE careful investigation of the alkaloids of the palmatine, berberine, corydaline type has not only demonstrated their *isoquinoline* structure, but has also shown that they are all built up on the same curious "angular" skeleton (I), a point which is made clear when the formula of berberine or, still better, of tetrahydroberberine (II) is written alongside.



Furthermore, the alkaloids cryptopine, protopine, and  $\beta$ -homochelidonine, although containing a ten-membered ring, are readily

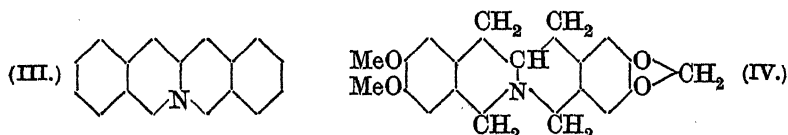
\* The Editor suggests that the substance



should be named "*paraberine*."



converted into quaternary salts, such as *isocryptopine* chloride, which again are derived from the skeleton (I). It is not clear why this particular angular structure should be selected as the basis of so many of the naturally occurring alkaloids, unless indeed it be that substances of this type are particularly amenable to synthesis. In order to obtain evidence on this point, it appeared to us that it would be of interest to synthesise an alkaloid of the paraberine type containing in the place of (I) the "linear" skeleton (III) and to compare the ease of formation and general properties of such a substance with those of the alkaloids met with in nature.

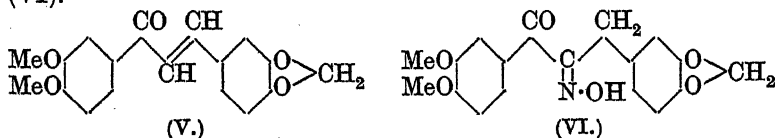


It will be seen from the experimental section of this communication that, although we were ultimately successful in constructing an alkaloid (IV) derived from the skeleton (III), the smallness of the yields at several stages made the completion of the synthesis a particularly difficult one. It is quite clear to us that substances of the angular type (I) are much more readily synthesised, under the conditions we have employed in this series of researches, than those of the linear type (III), and this fact may have some bearing on the occurrence of the angular type in nature. In attempting to synthesise (IV), the most obvious starting point was 6 : 7-dimethoxy-

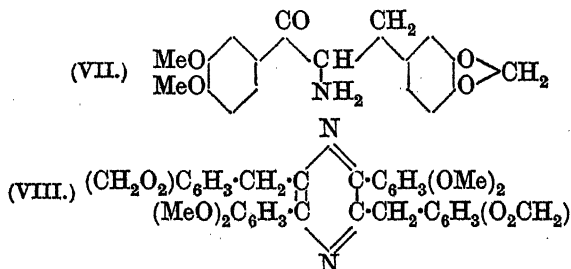
4-dihydroisoquinolone,  $C_6H_2(OMe)_2$   $\begin{matrix} \text{CO}-CH_2 \\ \text{CH}_2-NH \end{matrix}$ , but we were unable to obtain this substance either from  $\omega$ -aminoacetoveratrone,  $(MeO)_2C_6H_3-CO-CH_2-NH_2$ , by the action of formalin or from the *N*-formyl derivative of the base by treatment with phosphorus oxychloride. Moreover, *N*-phenacetyl- $\omega$ -aminoacetoveratrone (Robinson, J., 1909, 95, 2167), on treatment with phosphorus oxychloride, yielded not the *isoquinoline* derivative but 5-veratryl-2-benzylloxazole (m. p.  $86^\circ$ ), which Robinson had obtained from the phenacetyl derivative by the action of sulphuric acid. This failure to close the *isoquinoline* ring seems to indicate that it is the carbonyl group in  $\omega$ -aminoacetoveratrone which inhibits ring formation, because when this group is replaced by  $>CH_2$  or  $>CH-OH$  *isoquinoline* derivatives may be readily obtained (Pictet and Gams, *Ber.*, 1909, 42, 2943; Decker, *Annalen*, 1913, 395, 299). After many other unsuccessful attempts, we ultimately succeeded, with the aid of the following scheme, in synthesising 2 : 3-methylenedioxy-11 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine (IV).

3 : 4-Dimethoxyphenyl 3 : 4-methylenedioxyethyl ketone (V),

prepared from acetoveratrone and piperonal by Bargellini and Monti's method (*Gazzetta*, 1914, 44, ii, 25), was reduced by hydrogen in the presence of colloidal palladium to 3:4-dimethoxyphenyl 3:4-methylenedioxy- $\beta$ -phenylethyl ketone, which, on treatment with methyl nitrite and sodium ethoxide, yielded the isonitroso-derivative (VI).

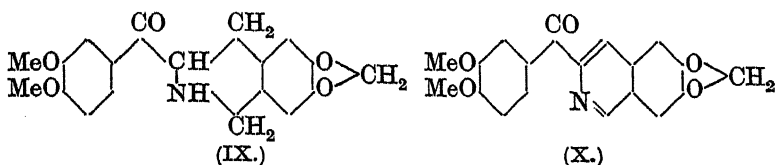


The reduction of this isonitroso-derivative to 3:4-dimethoxyphenyl 3:4-methylenedioxy- $\beta$ -phenyl- $\alpha$ -aminoethyl ketone (VII) proved to be a troublesome operation. When alkaline reducing agents were employed, the pyrazine derivative (VIII) was produced as the result of condensation between two molecules of the base (VII) followed by spontaneous oxidation. Eventually the amine (VII) was obtained by reducing the isonitroso-derivative (VI) with stannous chloride, but in order to obtain even approximately good yields the conditions described on p. 38 must be exactly followed.

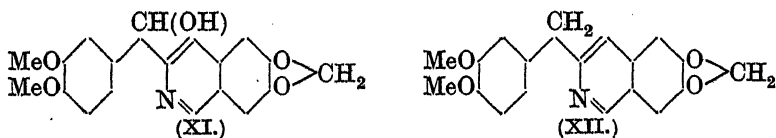


The amine (VII) condenses readily with formalin and hydrochloric acid to give 6:7-methylenedioxy-3-(3':4'-dimethoxybenzoyl)-1:2:3:4-tetrahydroisoquinoline (IX), the hydrochloride, oxime, picrate, and benzoyl derivative of which have been prepared. When the base (IX) is oxidised with iodine, it is converted into 6:7-methylenedioxy-3-(3':4'-dimethoxybenzoyl)isoquinoline (X), which is closely related to papaveraldine in structure and properties. It is a weak tertiary base yielding pale yellow salts which are slowly dissociated by water. On fusion with potassium hydroxide, it is decomposed and veratric acid has been isolated from the product, but the basic residue could not be identified, as it was no doubt destroyed during the fusion owing to disruption of the methylenedioxy-group. The formation of veratric acid is, however, welcome confirmation of the validity of the structures (IX) and (X) and it is evident that when the amine (VII) is condensed with formalin it

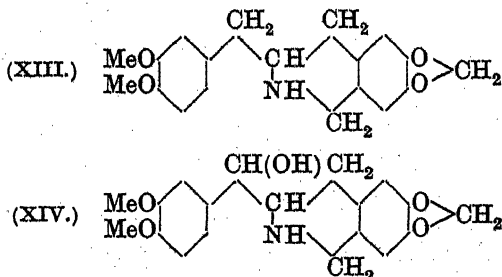
is again the  $>\text{CO}$  group which inhibits ring closure with the veratryl nucleus.



The base (X), on reduction with zinc dust and acetic acid, yields 6 : 7-methylenedioxy-3-( $\alpha$ -hydroxy-3' : 4'-dimethoxybenzyl)isoquinoline (XI), a secondary alcohol which shows reactions similar to those of papaverinol. When treated with hydrobromic acid and zinc dust (compare Buck, Perkin, and Stevens, J., 1925, 127, 1471), it yielded an oily base the crystalline picrate of which gave analytical figures agreeing with those required for the picrate of 6 : 7-methylenedioxy-3-(3' : 4'-dimethoxybenzyl)isoquinoline (XII), but owing to the small amount of material at our disposal we were unable to isolate the base in a pure state.



The reduction of the substances (IX), (X), and (XI) to 6 : 7-methylenedioxy-3-(3' : 4'-dimethoxybenzyl)-1 : 2 : 3 : 4-tetrahydroisoquinoline (XIII) proved to be a very difficult operation. Reducing agents such as sodium amalgam, zinc and sulphuric acid, as well as electrolytic reduction in the cold, led to the formation of amorphous bases. Since an exactly similar series of substances was obtained from papaveraldine and papaverinol under the same conditions, we are of the opinion that these amorphous bases are of the type (XIV).

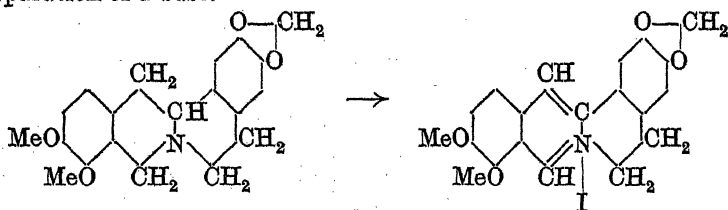


Freund and Beck (*Ber.*, 1904, 37, 3321) obtained an amorphous base, which they named "isotetrahydropapaverine," by the electrolytic reduction of papaveraldine in hot dilute sulphuric acid,

but Pyman (J., 1909, 95, 1610) showed that their base is identical with tetrahydropapaverine prepared by reducing papaverine with tin and hydrochloric acid. We have confirmed the identity of the two preparations by a careful comparison of the hydrochlorides, hydriodides, and nitrosoamines. When we applied the conditions employed by Freund and Beck to the electrolysis of the substance (X), we obtained the base (XIII) corresponding with tetrahydropapaverine. It is remarkable that this also is amorphous, but it yields a well-crystallised *hydrochloride*, *hydriodide*, and *nitrosoamine*.

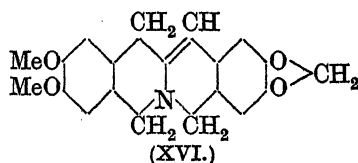
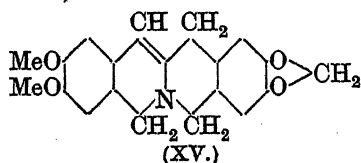
The base (XIII) is converted into 2:3-methylenedioxy-11:12-dimethoxy-6:15:16:17-tetrahydroparaberine (IV) by the action of formalin and hydrochloric acid, but the yield is extremely small and modifications of the process did not lead to any improvement. This experience appears to indicate that the system of rings (III) is produced only with difficulty and when compared with the ease of formation of substances of the tetrahydroberberine type under the same conditions clearly emphasises the greater tendency towards angular ring formation (I) (compare Lellmann and Schmidt, *Ber.*, 1887, 20, 3154; von Braun, *ibid.*, 1922, 55, 1710; Mayer and Schnecko, *ibid.*, 1923, 56, 1408).

In spite of the poor yield we have been able to examine the properties of the base (IV) in some important directions. It was to be expected that, owing to analogy in constitution, the base (IV) would exhibit properties closely allied to those of tetrahydroberberine and still more to those of tetrahydro- $\psi$ -berberine (Haworth, Perkin, and Rankin, J., 1924, 125, 1696). The latter two are characterised by the facility with which they crystallise as well as by the sparing solubility of their salts. But the most striking characteristic is their behaviour on oxidation with iodine, when they yield quaternary salts such as berberinium iodide or  $\psi$ -berberinium iodide (*loc. cit.*, p. 1698) which are not decomposed by alkali with separation of a base.



2:3-Methylenedioxy-11:12-dimethoxy-6:15:16:17-tetrahydroparaberine (IV; m. p. 222°) resembles tetrahydroberberine (m. p. 168°) and tetrahydro- $\psi$ -berberine (m. p. 177°) in being rather sparingly soluble and yielding sparingly soluble, beautifully crystalline salts. The *methiodide* (m. p. 268°), like tetrahydroberberine

methiodide (m. p.  $251^{\circ}$ ) and tetrahydro- $\psi$ -berberine methiodide (m. p.  $260^{\circ}$ ), exhibits remarkable stability to boiling alcoholic potassium hydroxide. On the other hand, when it is treated with iodine, base (IV) does not undergo a change corresponding with the conversion of tetrahydro-berberine or - $\psi$ -berberine into the quaternary berberinium salts. The product consists mainly of a bright yellow, crystalline *hydriodide*,  $C_{20}H_{19}O_4N.HI$ , from which the corresponding *hydrochloride* is obtained by the action of silver chloride, and the latter, in contact with ammonia, is immediately decomposed with separation of an amorphous base,  $C_{20}H_{19}O_4N$ , which is clearly a 2:3-methylenedioxy-11:12-dimethoxydihydroparaberine (6:17 or 6:15) having one or other of the constitutional formulæ (XV and XVI).



The reason for this difference in behaviour is difficult to understand, since the formula of base (IV) contains the grouping which is responsible for the formation of berberinium salts in the berberine series.

#### EXPERIMENTAL.

3:4-Dimethoxyphenyl 3:4-Methylenedioxy- $\beta$ -phenylethyl Ketone.—3:4-Dimethoxyphenyl 3:4-methylenedioxy-styryl ketone (V) was obtained in quantitative yield from piperonal and acetoveratrone under the conditions described by Bargellini and Monti (*loc. cit.*), but in reducing large quantities of this substance the following method is more suitable than that of the above-mentioned investigators. The styryl ketone (50 g.), glacial acetic acid (500 c.c.), 3% palladium chloride (15 c.c.), and gum arabic (0.5 g. in a little water) were introduced into a flask, connected to the hydrogen supply and immersed in a water-bath at  $50-60^{\circ}$ . The flask was fitted with a vigorously acting air-tight mechanical stirrer, the air displaced, and the mixture stirred, when a rapid absorption of hydrogen took place for 2 hours. The hot, colourless solution was filtered, most of the solvent removed, with the aid of a column, under diminished pressure, and methyl alcohol added, when the residue set to a mass of white crystals (41 g.); these crystallised from methyl alcohol in white, woolly needles, m. p.  $102-103^{\circ}$  (B. and M., *loc. cit.*, give  $98-100^{\circ}$ ). The *oxime*, prepared by boiling the phenylethyl ketone with potassium acetate and hydroxylamine hydrochloride in alcoholic solution, crystallised from aqueous alcohol in slender needles, m. p.

119—121°. The *isonitroso*-derivative (VI) was obtained by adding the phenylethyl ketone (10 g.) to boiling alcohol (200 c.c.) in which sodium (2.5 g.) had been dissolved. The hot solution was treated with a stream of dry methyl nitrite (Slater, J., 1920, **117**, 587), cooled, completely saturated with methyl nitrite, and kept in a stoppered flask for 12 hours at the room temperature, when a small amount of solid separated. Most of the alcohol was removed under diminished pressure, the residue diluted with water, and impurities extracted with benzene. Air was drawn through the aqueous layer, which was then rendered slightly acid with acetic acid, the precipitate collected,\* dried (8 g.), and crystallised from aqueous acetic acid, separating in colourless needles, m. p. 137° (Found: C, 62.9; H, 5.1; N, 4.3.  $C_{18}H_{17}O_6N$  requires C, 62.9; H, 5.0; N, 4.1%). This *isonitroso*-derivative is soluble in alcohol, chloroform, or ethyl acetate, slightly soluble in ether, and sparingly soluble in water or petroleum. An attempt to reduce it with zinc dust and acetic acid at 60° led to the regeneration of the phenylethyl ketone (m. p. 102—103°).

*3:4-Dimethoxyphenyl 3:4-Methylenedioxy-β-phenyl-α-aminoethyl Ketone* (VII).—Anhydrous stannous chloride (56 g.) dissolved in absolute alcohol (300 c.c.) was saturated with dry hydrogen chloride at -10°, the finely powdered *isonitroso*-derivative (40 g.) added, and the solution again saturated with hydrogen chloride at -10°. After remaining over-night, the crystalline *stannichloride* of the base (VII) which had separated was collected, dissolved in water, decomposed with hydrogen sulphide, filtered, and the filtrate concentrated until the hydrochloride separated as an oil which rapidly hardened. This (40 g.) was crystallised from a mixture of alcohol and ether, separating in slender, colourless needles, m. p. 218—219° (decomp.) (Found: C, 59.5; H, 5.5.  $C_{18}H_{18}O_5N \cdot HCl$  requires C, 59.9; H, 5.5%). This *hydrochloride* is sparingly soluble in cold alcohol, but dissolves readily in water or warm alcohol. The *picrate* was prepared in alcoholic solution and crystallised from alcohol in yellow needles, m. p. 213° (Found: C, 51.7; H, 4.1.  $C_{24}H_{22}O_{12}N_4$  requires C, 51.6; H, 3.9%). When sodium hydroxide is added to the aqueous solution of the hydrochloride, a turbid solution is first produced and after some time a brown, sticky solid separates which is evidently produced by the base undergoing condensation and oxidation to the pyrazine (VIII).

The *pyrazine* (VIII) is best prepared by stirring a solution of the *isonitroso*-derivative (VI) in sodium hydroxide with zinc dust

\* The mother-liquors contain a little *isonitroso*-compound together with some veratric acid, evidently produced by the hydrolysis of some of the *isonitroso*-derivative.

for 3 hours at the room temperature. The sticky solid which separates is extracted with chloroform, dried, the solvent removed, and the syrup crystallised from a mixture of alcohol and chloroform, when pale yellow needles, m. p.  $205^{\circ}$ , are obtained (Found : C, 69.0; H, 5.2.  $C_{36}H_{32}O_8N_2$  requires C, 69.6; H, 5.2%). This pyrazine is insoluble in alkali and is a weak base dissolving in concentrated hydrochloric acid, from which it is precipitated by dilution with water.

6 : 7-Methylenedioxy-3-(3' : 4'-dimethoxybenzoyl)-1 : 2 : 3 : 4-tetrahydroisoquinoline (IX).—A solution of the hydrochloride of the amine (VII) (2 g.) in methyl alcohol (25 c.c.) and 40% formalin (5 c.c.) was decomposed with sodium bicarbonate, boiled for 20 minutes, diluted with water, and the reddish-brown condensation product collected, washed free from formalin, and digested on the steam-bath with 20% hydrochloric acid. The mass dissolved and in a few minutes the hydrochloride of the base (IX) began to separate, the quantity increasing during 20 minutes. The mixture was cooled, the hydrochloride collected, washed with water, and re-crystallised from very dilute hydrochloric acid. It was then dissolved in water and the base liberated by the addition of ammonia, collected, and crystallised from ethyl alcohol, from which it separates in rosettes of almost colourless needles, m. p.  $137^{\circ}$  (Found : C, 67.2; H, 5.7.  $C_{19}H_{19}O_5N$  requires C, 66.9; H, 5.5%). The base (IX) is readily soluble in chloroform, acetone, hot alcohol, or hot benzene, and sparingly soluble in ether, petroleum, cold alcohol, or cold benzene. It dissolves in concentrated sulphuric acid to a pale yellow solution, which becomes blood-red on the addition of a crystal of potassium nitrate. The hydrochloride crystallises from very dilute hydrochloric acid in slender needles containing water of crystallisation, which is lost at  $115$ – $120^{\circ}$ . The hydrated salt is very soluble in alcohol and the addition of ether to an alcoholic solution precipitates the anhydrous hydrochloride in fine needles, m. p.  $232$ – $234^{\circ}$  (decomp.), which are now insoluble in alcohol. The hydrated salt dried at  $120^{\circ}$  lost 9.7%  $H_2O$ ;  $C_{19}H_{20}O_5NCl \cdot 2H_2O$  requires  $H_2O$ , 8.7% (Found : C, 60.0; H, 5.5.  $C_{19}H_{20}O_5NCl$  requires C, 60.4; H, 5.3%). The benzoyl derivative, obtained by the action of benzoyl chloride and sodium hydroxide on a solution of the hydrochloride, crystallises from alcohol in long, slender needles, m. p.  $187$ – $188^{\circ}$  (Found : C, 69.7; H, 5.2.  $C_{26}H_{23}O_6N$  requires C, 70.1; H, 5.2%). The picrate, prepared from an alcoholic solution of the hydrochloride, crystallises from alcohol in yellow needles containing solvent of crystallisation, m. p.  $157$ – $158^{\circ}$  (decomp.) (Found : C, 50.9; H, 4.5.  $C_{25}H_{22}O_{12}N_4 \cdot H_2O$  requires C, 50.9; H, 4.1%). The oxime was obtained by heating the hydro-

chloride with hydroxylamine hydrochloride for 1 hour in pyridine solution. The mixture was diluted with water and saturated with carbon dioxide; the oxime then slowly separated in needles, m. p. 205—209° (decomp.).

6 : 7-Methylenedioxy-3-(3' : 4'-dimethoxybenzoyl)isoquinoline (X).—The base (IX) (2 g.) was dissolved in ethyl alcohol (50 c.c.) containing potassium acetate (2 g.) and the solution boiled for  $\frac{1}{2}$  hour during the gradual addition of a 2% alcoholic solution of iodine (200 c.c.). On cooling, a mass of crystals separated which were collected, washed with sulphurous acid, water, and alcohol and crystallised from 50% alcoholic glacial acetic acid, separating in colourless needles, m. p. 222° (Found : C, 67.1; H, 4.5.  $C_{19}H_{15}O_5N$  requires C, 67.6; H, 4.4%). This substance (X) is sparingly soluble in alcohol, but readily soluble in glacial acetic acid or chloroform. It is insoluble in water, but dissolves in warm dilute hydrochloric acid to a yellow solution, from which the free base separates on cooling. The *sulphate* crystallises from 20% sulphuric acid in pale yellow plates which slowly dissociate on washing with water. The *oxime* was obtained by boiling an alcoholic solution of the base (X) with hydroxylamine hydrochloride and potassium acetate for 8 hours. The solid was collected and washed with water, when the oxime remained as slender, colourless needles, m. p. 234—236° (decomp.). The base (X) (1 g.) was fused at 180° with potassium hydroxide (10 g.) and a little water. After 5 minutes the brown mass was dissolved in water, the black solution saturated with carbon dioxide, and the brown, amorphous precipitate collected. The filtrate was acidified, extracted with chloroform, the extract dried, and the solvent removed, when a brown solid remained. This was warmed with sodium bicarbonate solution, filtered, the filtrate acidified, the solid collected and crystallised from hot water containing animal charcoal, when needles, m. p. 178°, were obtained which were identified as veratric acid.

6 : 7-Methylenedioxy-3-( $\alpha$ -hydroxy-3' : 4'-dimethoxybenzyl)isoquinoline (XI).—The substance (X) (2 g.) dissolved in glacial acetic acid (20 c.c.) was heated on a water-bath during the gradual addition of zinc dust (0.4 g.). After 4 hours, the solution was filtered, the filtrate diluted with water, allowed to remain for some time, and the small precipitate of unchanged (X) removed. The filtrate was saturated with hydrogen sulphide, the zinc sulphide removed, the filtrate concentrated and made alkaline with concentrated ammonia, when a sticky solid separated which gradually hardened. This was collected, and crystallised from alcohol in colourless needles, m. p. 153° (Found : C, 67.4; H, 5.1.  $C_{19}H_{17}O_5N$  requires C, 67.3; H, 5.0%). This base (XI) is insoluble in water, sparingly soluble



in cold alcohol, but readily soluble in hot alcohol, acetone, or chloroform. It dissolves in concentrated sulphuric acid to a magenta-coloured solution, which becomes deep green on the addition of a crystal of potassium nitrate. The *picrate* separated as an oil which rapidly hardened when an alcoholic solution of the base (XI) was treated with picric acid. It crystallises from much alcohol in yellow needles which darken at  $183^{\circ}$  and melt at  $195^{\circ}$  (decomp.) (Found: C, 53.1; H, 3.7.  $C_{25}H_{20}O_{12}N_4$  requires C, 52.8; H, 3.5%).

6 : 7-Methylenedioxy-3-(3' : 4'-dimethoxybenzyl)isoquinoline (XII).—The base (XI) (0.5 g.) was allowed to remain for 12 hours in glacial acetic acid (5 c.c.) saturated with hydrogen bromide. The solution was then heated to  $30^{\circ}$ , stirred, and excess of zinc dust added slowly during 3 hours. After filtration, the solution was diluted with water (50 c.c.), made alkaline with ammonia, extracted with chloroform, the extract dried and concentrated, when a thick syrup was obtained which did not crystallise. The *picrate* was prepared in alcoholic solution and crystallised from much alcohol in yellow needles, m. p.  $206-207^{\circ}$  (Found: C, 53.9; H, 3.7.  $C_{25}H_{20}O_{11}N_4$  requires C, 54.3; H, 3.6%). All attempts to decompose the *picrate* by digesting with ammonia or sodium hydroxide were unsuccessful.

6 : 7-Methylenedioxy-3-(3' : 4'-dimethoxybenzyl)-1 : 2 : 3 : 4-tetrahydroisoquinoline (XIII).—The substance (X) (4 g.) was suspended in 10% sulphuric acid (200 c.c.) and placed in an enamelled metal can, which constituted the cathode compartment of an electrolytic cell. The solution was heated to  $90-95^{\circ}$  and subjected to a current of 10 amperes, when the suspended sulphate gradually dissolved to a yellow solution which became colourless after 2 hours. The hot solution was filtered, made alkaline with strong ammonia, and extracted with chloroform; a red syrup remained on removing the solvent. This was extracted with boiling dilute hydrochloric acid, the solution filtered, and the filtrate treated with solid potassium iodide, when a sticky *hydriodide* separated which gradually hardened on cooling. This separated from alcohol, in which it was sparingly soluble, in small crystals, m. p.  $226^{\circ}$  (decomp.) (Found: C, 50.2; H, 5.0.  $C_{19}H_{21}O_4N_4HI$  requires C, 50.1; H, 4.8%). The *hydrochloride*, obtained by digesting an aqueous solution of the *hydriodide* with silver chloride, crystallised from alcohol in small needles, m. p.  $220-222^{\circ}$  (decomp.). The *nitrosoamine* separated, on the addition of sodium nitrite to a solution of the *hydrochloride*, as an oil which hardened, and crystallised from alcohol in short needles, m. p.  $128^{\circ}$  (Found: C, 63.8; H, 5.7.  $C_{19}H_{20}O_5N_2$  requires C, 64.0; H, 5.6%).

2 : 3-Methylenedioxy-11 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydro-*paraberine* (IV).—The *hydriodide* of the base (XIII) (2 g.), dissolved

in methyl alcohol (10 c.c.), was decomposed with sodium bicarbonate and boiled for a few minutes with 40% formalin solution (10 c.c.). The mixture was cooled, diluted with water, sodium chloride added, and the solution decanted from the semi-solid mass which had separated. The latter was well washed with water, digested with concentrated hydrochloric acid (10 c.c.) on the steam-bath for a few minutes, diluted with water, and made alkaline with ammonia; an oil then separated which rapidly hardened. This was collected, triturated with methyl alcohol (15 c.c.), and the insoluble, colourless base (IV) (0.3 g.) collected and crystallised from benzene, from which it separated in small, colourless prisms, m. p. 221—222° (Found: C, 70.8; H, 6.4.  $C_{20}H_{21}O_4N$  requires C, 70.8; H, 6.2%). The base (IV) is insoluble in water, sparingly soluble in ether, petroleum, or cold alcohol, moderately easily soluble in warm alcohol or benzene, and readily soluble in chloroform. The *hydrochloride* crystallises from water, in which it is fairly soluble, in small, colourless needles, m. p. 236—238°. The *picrate*, prepared in alcoholic solution, crystallises from alcohol in yellow nodules, m. p. 199—201° (decomp.) (Found: C, 54.5; H, 4.3.  $C_{26}H_{24}O_{11}N_4$  requires C, 54.9; H, 4.2%). The *methiodide* was prepared by boiling a benzene solution of the base (IV) with an excess of methyl iodide for 1 hour, the solvent removed, and the residue crystallised from methyl alcohol, separating in large prisms, m. p. 268° (Found: C, 52.2; H, 5.2.  $C_{21}H_{24}O_4NI$  requires C, 52.4; H, 5.0%). This methiodide was boiled with a large excess of 25% methyl-alcoholic potassium hydroxide for 6 hours, but, on cooling, crystals of the unchanged methiodide separated and no other substance could be isolated from the product. The methiodide was digested for 3 hours with an aqueous suspension of silver chloride and filtered, when the *methochloride* separated as a gelatinous precipitate, m. p. 260° (decomp.), from the filtrate. The methochloride was recovered after boiling for 6 hours with 25% methyl-alcoholic potassium hydroxide.

2 : 3-Methylenedioxy-11 : 12-dimethoxy-6 : 17 or -6 : 15-dihydro-*paraberine* (XV or XVI).—The base (IV) (1 g.), dissolved in alcohol (20 c.c.) containing potassium acetate (1 g.), was treated with a 1% alcoholic solution of iodine (200 c.c.). After boiling for  $\frac{1}{2}$  hour, the mixture was cooled, and the crystalline periodide was collected and converted, by the action of sulphurous acid, into the bright yellow hydriodide; this was collected, boiled with water and the solution filtered hot. The residue consisted of a high-melting, orange-coloured hydriodide, the yield of which was too small to allow of detailed investigation. A small quantity, however, was converted into the hydrochloride by means of silver chloride, and this

gave an immediate precipitate with ammonia, showing that it was not a quaternary salt. The filtrate, on cooling, deposited pale yellow needles, m. p. 225—226° (Found: C, 51.5; H, 4.4.  $C_{20}H_{19}O_4N$ , HI requires C, 51.6; H, 4.3%). This *hydriodide* is sparingly soluble in cold water or cold alcohol, but moderately soluble in the warm solvents. The *hydrochloride* was obtained by digesting an aqueous solution of the hydriodide with silver chloride and separated from a little water in bright yellow needles which melted at 120° with loss of water of crystallisation. On drying at 120°, it lost 11.5%  $H_2O$  (Found: C, 63.3; H, 5.5.  $C_{20}H_{19}O_4N \cdot HCl \cdot \frac{1}{2}H_2O$  requires C, 62.9; H, 5.5%). The *base* (XV or XVI) was obtained as a pale yellow, amorphous, gelatinous precipitate by the addition of ammonia to an aqueous solution of the hydrochloride, and was collected and dried. It was soluble in the usual organic solvents with the exception of petroleum, but it could not be obtained in the crystalline state. The addition of petroleum (b. p. 40—60°) to the dry ethereal solution precipitated the base as a pale yellow, amorphous powder melting indefinitely between 180° and 190° (Found: C, 70.9; H, 5.7.  $C_{20}H_{19}O_4N$  requires C, 71.2; H, 5.6%).

One of us (R. C.) is indebted to the Trustees of the Earl Grey Memorial Fellowship of Armstrong College, Newcastle-on-Tyne, for a fellowship, and another (R. D. H.) to the Commissioners of the 1851 Exhibition for a studentship. Our thanks are also due to the Research Fund Committee of the Chemical Society and to the Government Grant Committee of the Royal Society for grants which have defrayed some of the expense of this investigation.

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## X.—Keto-enol Isomerism of Ethylenebisacetylacetone.

By GILBERT T. MORGAN and CYRIL JAMES ALLAN TAYLOR.

IN their reactions with inorganic reagents acetylacetone and its homologues exhibit the behaviour of three dynamic isomerides: (1) a diketonie form manifested in condensation with tellurium tetrachloride, (2) a *trans*-monoenolic form with selenium tetrachloride, and (3) a *cis*-monoenolic modification with copper acetate, ferric chloride and other metallic salts (Morgan and Drew, J., 1924, 125, 1044).

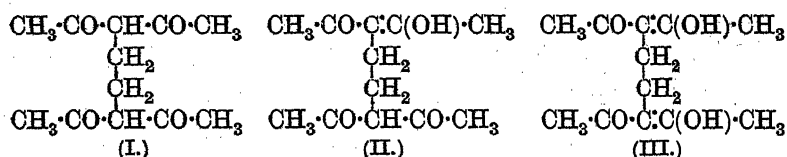
Ordinary acetylacetone consists principally of enolic forms and in 1921 K. Meyer and Hopff, by distilling the diketone under reduced pressure in silica vessels, succeeded in separating the

enolic and keto-forms, which, however, reverted rapidly to the equilibrium mixture (*Ber.*, 1921, 54, 579).

With certain derivatives of acetylacetone the individual modifications are more stable. Thus Knoevenagel (*Ber.*, 1903, 36, 2150) indicated two isomeric forms of methylenebisacetylacetone, one a solid and the other an oil, both of which developed deep violet colorations with ferric chloride. He regarded the oil as the dienolised form, since with ammonia it yielded diacetyldihydrolutidine, whereas the solid, which gave no dihydropyridine derivative with ammonia, he regarded as the mono-enolised compound.

Schiff claimed to have isolated no fewer than six isomeric varieties of benzylidenebisacetylacetone, namely, a keto-form, two mono-enols (*cis* and *trans*) and three dienols (*dicis*, *ditrans* and *cis-trans*). He did not, however, characterise these various modifications (*Annalen*, 1899, 309, 206).

In the present communication, ethylenebisacetylacetone, prepared by the condensation of sodium acetylacetone and ethylene dibromide, is shown to exist in at least three isomeric forms, which have been identified definitely as a keto-form (I), a mono-enolic modification (II), and a dienolic variety (III).



1. keto-*Ethylenebisacetylacetone* (I) is a mobile, colourless liquid of high boiling point; its alcoholic solution only slowly develops a violet colour with ferric chloride.

2. mono-enol-*Ethylenebisacetylacetone* (II) is obtained in prismatic crystals, m. p. 99°; its alcoholic solution develops instantaneously a deep violet coloration with ferric chloride.

3. dienol-*Ethylenebisacetylacetone* (III) separates in cubical crystals, m. p. 140–143°, and reacts immediately with ferric chloride. This form is, however, less stable in air than the preceding varieties and the melting point of the crystals soon falls to about 100–110°.

The foregoing isomerides were characterised by an application of Meyer's method for estimating the percentage of enolic modification in a tautomeric substance such as acetylacetone (*Annalen*, 1911, 380, 212; 1913, 398, 49; *Ber.*, 1911, 44, 2718; 1912, 45, 2843), which depends on the rapid addition of bromine to the enolic modification, but not to the ketonic form. When treated with excess of hydroxylamine, keto-ethylenebisacetylacetone and enol-

ethylenebisacetylacetone both yield stereoisomeric tetraoximes. In the latter oximation, it is evident that hydroxylamine causes the enolic modification to revert to the ketonic isomeride.

## EXPERIMENTAL.

*Interaction of Sodium Acetylacetone and Ethylene Dibromide.*—Sodium acetylacetone (210 g.) was mixed with excess of ethylene dibromide (600 g.) and refluxed at 160° for 12 hours; the mixture was then allowed to cool and the deposit of sodium bromide washed with ether. The weight of bromide corresponded nearly quantitatively with the amount of sodium originally in the sodium acetylacetone.

The brown ethereal filtrates were distilled, ether and ethylene dibromide being collected up to 135° and acetylacetone from 135° to 145°; the residue was transferred to a Claisen flask and distilled under reduced pressure (3—5 mm.), and the following fractions were collected: (1) b. p. 60—80°—contained the remainder of the ethylene dibromide and acetylacetone; (2) b. p. 80—100°—25 g. of a slightly yellow liquid boiling under ordinary pressure at about 200°. Its alcoholic solution gave no immediate coloration with ferric chloride, but a violet coloration slowly developed; it did not give a copper salt with ammoniacal copper acetate; (3) b. p. 120—130°—8.5 g. of a yellow oil; its alcoholic solution gave an immediate violet colour with ferric chloride and a small precipitate of copper salt with ammoniacal cupric acetate; (4) b. p. 170—200°—19 g. of a brown, viscid oil which gave an instantaneous ferric coloration and a copious precipitate with ammoniacal cupric acetate.

I. *keto-Ethylenebisacetylacetone* (I).—The principal product of the reaction, represented by the second fraction (b. p. 80—100°), was redistilled under reduced pressure, when about 80% distilled between 83° and 85°/4 mm. The resultant liquid was slightly yellow, readily miscible with water, alcohol, benzene, ether, or chloroform, but not with light petroleum; it dissolved in dilute sodium hydroxide to a yellow solution. A sodium salt was formed by adding metallic sodium to the liquid dissolved in ether.

After several distillations under reduced pressure, *keto-ethylenebisacetylacetone* boiled at 97—99°/20 mm. (Found: C, 63.3, 63.9; H, 7.9, 7.9.  $C_{12}H_{18}O_4$  requires C, 63.7; H, 8.0%).

II. *Dehydration Product of Ethylenebisacetylacetone.*—The third fraction (b. p. 120—130°) did not solidify on keeping in the ice chest and was therefore dissolved in alcohol and treated with an excess of ammoniacal cupric acetate, when on dilution with water a small amount of copper salt was precipitated, but the major part of the substance evidently remained dissolved in the aqueous-

alcoholic filtrate. By diluting further with water and extracting several times with ether, a light brown oil was obtained, which soon crystallised. After repeated crystallisation from alcohol, the substance separated in colourless, hexagonal plates or laminae, but only a very small amount was isolated. Its alcoholic solution did not respond to ferric chloride (Found: C, 72.2, 72.4; H, 8.2, 7.3.  $C_{24}H_{30}O_5$  requires C, 72.4; H, 7.5%, thus corresponding with a possible dehydration product of ethylenebisacetylacetone:  $2C_{12}H_{18}O_4 - 3H_2O = C_{24}H_{30}O_5$ ) (Knoevenagel, *loc. cit.*).

III. enol-Ethylenebisacetylacetone (II).—The fourth fraction (b. p. 170—200°) was cooled in ice, when crystallisation set in. The first deposit consisted of a mass of needles which, after washing with a little ether, were colourless and melted at 134°. Recrystallisation from alcohol or benzene gave a product with indefinite melting point, liquefaction commencing at about 100°, but not being complete until 130°. Its alcoholic solution gave an intense violet colour with ferric chloride and a copper derivative with ammoniacal cupric acetate.

When left in the ice chest for several days, the mother-liquors deposited prismatic crystals; these, when washed free from oil with the aid of ether, melted at 98—99°. Recrystallisation from benzene gave a mass of glistening, white needles, m. p. 99—100°; recrystallisation from alcohol also gave very fine needles melting at 99°. A mixture of the original crystals with those obtained after recrystallisation from alcohol and from benzene also melted at 98°, which indicated a definite substance and not a mixture (Found: C, 63.6, 63.7; H, 8.0, 8.2.  $C_{12}H_{18}O_4$  requires C, 63.7; H, 8.0%).

This monoenol-ethylenebisacetylacetone (p. 44) when dissolved in alcohol gave an instantaneous deep violet coloration with ferric chloride and a precipitate of a copper salt with ammoniacal cupric acetate. After keeping for some months, its melting point became 146—152°.

IV. dienol-Ethylenebisacetylacetone (III).—The mother-liquors from the crystals of the monoenol showed no further signs of crystallisation and were converted into the copper derivative by treating an alcoholic solution with excess of ammoniacal cupric acetate. After drying, the mass was extracted with benzene; a faintly yellow solution was obtained which on evaporation of the solvent left a few drops of a brown oil, whilst the copper salt remained as an insoluble greenish-grey powder. It had no definite melting point, but decomposed above 250°, and was quite insoluble in all organic solvents. It contained 18% of copper.  $C_{24}H_{34}O_8Cu$  requires Cu, 12.3 and  $C_{12}H_{16}O_4Cu$  requires Cu, 22.1%.

The copper salt was decomposed with sulphuric acid in the presence of ether; a white precipitate was formed and was filtered off, whilst the ethereal layer was allowed to evaporate. The insoluble product with indefinite melting point of 100—107° was subsequently shown to be a mixture of mono- and di-enolic forms. The product separating from the ethereal layer formed colourless, cubic crystals which after washing with ether melted more definitely at 140—143° and consisted chiefly of dienol-*ethylenebisacetylacetone* (Found: C, 63.6; H, 7.9.  $C_{12}H_{18}O_4$  requires C, 63.7; H, 8.0%).

When kept for some time, the melting point of the dienol became indefinite; melting commenced at 100°, but was not complete until about 140°. This change in fusibility probably indicated a partial transformation into a mixture of the mono- and di-enolic forms.

V. *Comparative Study of the Behaviour of the Three Isomerides towards Bromine*.—A known weight of the isomeride under investigation, dissolved in sufficient alcohol to give an approximately *M*/20-solution, was treated with *N*/10-bromine (alcoholic) in the cold until the yellow colour persisted; an alcoholic solution of  $\beta$ -naphthol was then quickly added to absorb the excess of bromine. Potassium iodide was added and the solution gently warmed; iodine was liberated and titrated by means of *N*/10-thiosulphate without the use of an indicator, 1 g.-mol. of iodine being equivalent to one double bond, that is, to one hydroxyl group.

(a) *The liquid keto-ethylenebisacetylacetone*: 1 g.-mol. liberates  $0.033 \times 127$  g. of iodine, corresponding with the presence of about 0.8% of the enolic form.

(b) *enol-Ethylenebisacetylacetone*, m. p. 98—99°: 1 g.-mol. liberates  $2 \times 127$  g. of iodine, corresponding with the pure mono-enolic form of ethylenebisacetylacetone.

(c) *dienol-Ethylenebisacetylacetone*, m. p. 140—143°: 1 g.-mol. liberates  $2.5 \times 127$  g. of iodine; this indicates the presence of about 1.25 hydroxyl groups per g.-mol. or a mixture of 25% of the dienolic with 75% of the mono-enolic form of ethylenebisacetylacetone.

From these results, we conclude that in the case of the liquid and the solid, m. p. 98°, we are dealing with the comparatively stable ketonic and mono-enolic forms of ethylenebisacetylacetone, respectively. The other product, m. p. 140—143°, may be an equilibrium mixture; or more probably it represents in the solid state the true dienolic form, which in alcoholic solution becomes transformed into an equilibrium mixture.

*Comparative Study of the Ketonic and Monoenolic Forms of Ethylenebisacetylacetone*.—*Stereoisomeric tetraoximes*. The liquid *keto*-ethylenebisacetylacetone and the solid enol modification were each heated on the water-bath for 2 hours in dilute alcohol with

excess of hydroxylamine hydrochloride (6—8 mols.) and sodium acetate. On the mixture being poured into water, the  $\alpha$ -tetraoxime from the keto-form remained in solution, and was extracted with ether. It separated from the concentrated ethereal extract in colourless crystals, m. p.  $165^{\circ}$  (Found: N, 19.15.  $C_{12}H_{22}O_4N_4$  requires N, 19.6%).

The  $\beta$ -tetraoxime from the enol form separated as a white solid crystallisable from hot water in minute, colourless needles decomposing at  $220$ — $222^{\circ}$  (Found: N, 19.7%).

*Tellurium Tetrachloride and keto-Ethylenebisacetylacetone.*—The liquid keto-form (9 g. = 2 mols.) and 5.4 g. (1 mol.) of tellurium tetrachloride were refluxed in chloroform solution. The mixture immediately blackened, but little or no hydrogen chloride was evolved until after  $\frac{1}{2}$  hour; the gas was then freely evolved during 3 hours. The filtrate from tellurium (0.4 g.) was concentrated in a vacuum desiccator. A black tar remained; no crystallisation took place even after one month or on treatment with various solvents. On extraction with *n*-hexane, the tar remained undissolved, but after evaporation of the hydrocarbon crystalline laminae were left. By pressing these on a porous plate, white crystals were obtained, which were purified by crystallisation from hexane. Hexagonal prisms resulted, m. p.  $79^{\circ}$ , yield 1 g. The product was readily soluble in alcohol and the solution gave an immediate intense purple colour with ferric chloride; it also yielded a copper salt. Qualitative tests showed the absence of tellurium, but chlorine was present and could be detached by boiling with aqueous potash (Found: C, 52.0, 51.6; H, 7.0, 6.9.  $C_7H_{11}O_2Cl$  requires C, 51.7; H, 6.8%). This analysis corresponds with a removal of one acetylacetone residue and the formation of  $\beta$ -chloroethylacetylacetone,  $CH_2Cl \cdot CH_2 \cdot CH(CO \cdot CH_3)_2$ .

*Transformations of enol-Ethylenebisacetylacetone into its Isomerides.*—*Ketonisation.* The mono-enol formed stable, prismatic crystals, m. p.  $99^{\circ}$ . It was slightly soluble in water and the solution reacted faintly acid to litmus. It readily dissolved in dilute caustic soda to a yellow solution of the sodium salt; no precipitate was produced when this solution was acidified with sulphuric acid in the cold, and extraction with ether yielded an oil which failed to colour ferric chloride and was probably the ketonic form.

*Dienolisation.* The copper salt, prepared from the mono-enolic form by treating a solution in alcohol with excess of ammoniacal cupric acetate, dried to an amorphous, greenish-grey powder quite insoluble in all organic solvents, thus differing from the usual co-ordinated copper derivatives obtained from the  $\beta$ -diketones. It contained 19.3% of copper; the amount calculated for the copper



derivative of the monoenol is 12.3, and for that of the dienol 22.1%. When decomposed in the usual manner with sulphuric acid in the presence of ether, an amorphous, white solid is precipitated which is only sparingly soluble in ether; after washing with ether and drying, this melts at 98° and is the monoenolic form, but the substance which crystallises from the ethereal solution has an indefinite melting point; it softens and loses its crystalline form at 110°, but does not run down the tube to a clear liquid until 130—134°, behaving as a mixture of the di- and mono-enolic forms; Meyer's test indicates the presence of about 20% of the dienolic form with 80% of the monoenolic. It is evident that under the influence of ammoniacal cupric acetate the monoenol changes partly to the dienol.

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## XI.—*The Solubilities of Sodium, Potassium, and Calcium Ferrocyanides. Part I.*

By MONICA FARROW.

THIS investigation was undertaken on account of the uncertainty of the solubility data for the ferrocyanides of sodium and potassium, and the lack of data for the calcium salt. Early workers, e.g., Michel and Kraft (*Ann. Chim. Phys.*, 1854, **41**, 482), Étard (*ibid.*, 1894, **2**, 546), and Schiff (*Annalen*, 1860, **113**, 350), obtained values varying from 25 to 40 g. of potassium ferrocyanide in 100 g. of water at 20°. Determinations for the potassium and sodium salts were made at a few temperatures by Conroy (*J. Soc. Chem. Ind.*, 1898, **17**, 104), by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2716) at 25° only, by Fabria (*Gazzetta*, 1921, **51**, ii, 374) over the whole range from the cryohydric point to 100°, and by Vallance (*Chem. News*, 1922, **125**, 7) for the potassium salt only, at low temperatures.

*Purification of the Salts.*—The purest sodium and potassium ferrocyanides obtainable were further purified by rapid crystallisation from hot water. By simple qualitative tests the absence of the most likely impurities, calcium and ammonium, was proved.

The purest calcium salt obtainable, for which we are indebted

to Mr. W. G. Adam of the Gas Light & Coke Co., was slightly tinged with blue. It was purified by precipitation with absolute alcohol in the cold (to avoid oxidation) from an air-free saturated solution. The pure lemon-yellow, finely crystalline product was centrifuged, dried in vacuum desiccators, first over charcoal for 24 hours, then over the partly dehydrated salt, and stored in the dark in dark glass-stoppered bottles. No discoloration appeared after 18 months. No trace of sodium, potassium, or ammonium could be detected in the residue left after decomposition of the salt with concentrated sulphuric acid. Determinations of calcium as oxalate in the original and the purified salt proved that no measurable change of composition had resulted from the purification process :

Orig. salt : 16.2, 16.2, 16.2, 16.3, 16.25, 16.1, 16.2, 16.2.  
Mean, 16.2% Ca.

Recryst. salt : 16.2, 16.25, 16.2, 16.2, 16.2, 16.2, 16.2, 16.3.  
Mean, 16.2% Ca.

There has been some doubt about the precise number of molecules of water in the calcium salt. The above determinations, which lie much nearer to the theoretical value for a hydration of  $11\text{H}_2\text{O}$  (16.3% Ca) than to that for  $12\text{H}_2\text{O}$  (15.8% Ca), support the conclusion of Berkeley, Hartley, and Burton (*Phil. Trans.*, 1908, 209A, 177) that the lower figure is correct. The lower figure is also in accordance with the recent careful determinations of Cumming (J., 1924, 125, 240).

*Method of Determining Solubility.*—A solution was heated in contact with excess of the solute to the required temperature and after the attainment of equilibrium a definite volume was withdrawn in a weight pipette to be weighed and analysed, and the density calculated.

The ferrocyanide in all three salts was estimated volumetrically with permanganate by the simple method of de Haen (Treadwell, "Quantitative Analysis," p. 632). This method after practice gave concordant results; it is essential to standardise the solution used against standard potassium ferrocyanide and not against the customary oxalic acid. The calcium ferrocyanide was also determined independently as oxalate.

Cumming's method of estimating ferrocyanides with benzidine hydrochloride (J., 1924, 125, 240) was tried, but it did not appear so suitable for these metallic ferrocyanides as the simple permanganate method and was therefore not employed.

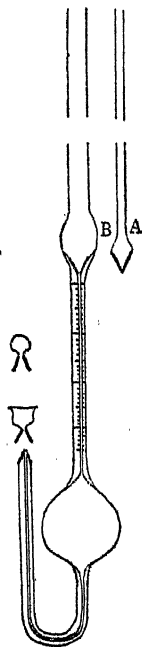
Pure dilute boiling sodium oxalate solution was used in the determination of the calcium salt as oxalate, because ammonium oxalate and oxalic acid as precipitants produced insoluble double calcium

ammonium ferrocyanide and insoluble hydroferrocyanic acid, respectively. In the first experiments, in which an alundum cone was used as a filter, no sharp end-point could be obtained on the addition of permanganate, owing to slow diffusion of oxalate from the inner pores of the cone. Gooch crucibles were substituted for the cones, but even then the permanganate readings were not concordant. The asbestos used had no reducing action on permanganate, and experiment also showed that no measurable occlusion occurred at the dilutions used. The cause of the error was traced to the appreciable solubility of calcium oxalate in water. The washing was therefore limited to three fillings of the Gooch, and this procedure was kept constant throughout the experiments.

*Apparatus.*—The solubility vessel consisted of a wide tube of about 200 c.c. capacity, fitted with a rubber bung and stirrer. In order to hold the pipette in place in the solubility vessel the bung carried a short glass tube which was closed when not in use. The temperature of the thermostat was constant to within  $0.2^{\circ}$ .

The weight pipette, which had a volume of about 4.5 c.c. (Fig. 1), was of a design which has been used for several investigations in this laboratory, but has not previously been described. It is warmed to the temperature of experiment and introduced into the solution with its shorter arm fitted with a glass-wool filter adapted to the ground end. The solution can then be admitted by opening the ground-in plug, A; when it has reached the required level, which can be accurately read by means of the graduations, the plug is replaced. The pipette is then removed, the filter immediately replaced by a ground-on cap, and the whole cleaned and weighed after attaining room temperature. The pipette was repeatedly calibrated with pure mercury to give accurate volume readings for the density determinations.

FIG. 1.



Owing to the high solubilities of the calcium salt, these solutions were very viscous and consequently difficult to introduce into the pipette. To hasten the filling, slight pressure was applied to the solution in the solubility vessel. The determinations of solubility and density were in almost every case repeated at least once, and, as the data of the table show, the individual solubility experiments very seldom differed from the mean by more than 0.1 unit, or the densities by more than 0.002, except at the highest temperatures,

when the experimental difficulties already mentioned make the determinations somewhat less concordant.

*Solubilities and Densities.*

*g* = grams of anhydrous salt in 100 grams of solution. *d* = density of saturated solutions. The mean values are printed in italics.

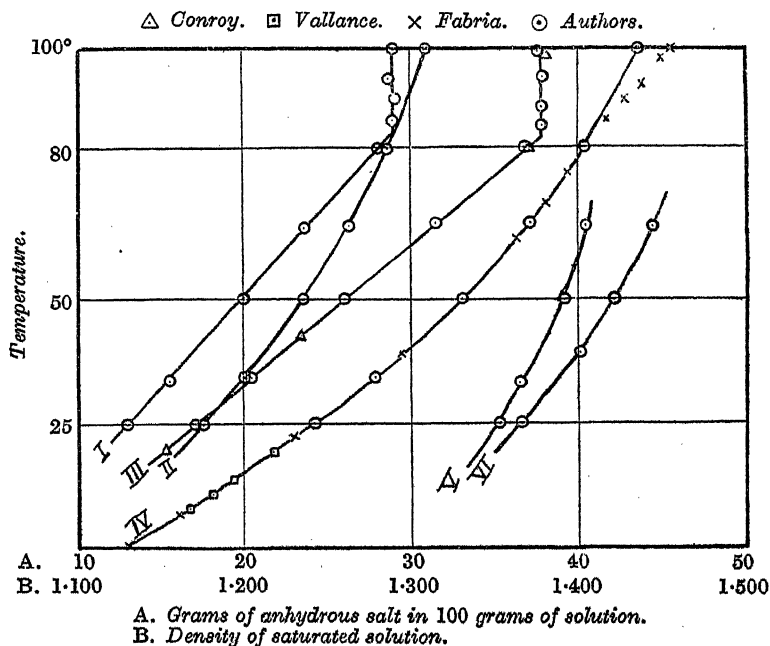
Temp.	$K_4Fe(CN)_6$		$Na_4Fe(CN)_6$		$Ca_2Fe(CN)_6$	
	<i>g.</i>	<i>d.</i>	<i>g.</i>	<i>d.</i>	<i>g.</i>	<i>d.</i>
24.9°	23.96	1.1731	17.10	1.1330	36.52	1.3574
	23.83	1.1731	17.15	1.1295	36.42	1.3552
	24.00	1.1734	17.08	1.1312	36.45*	1.3563
	24.01	1.1729	17.11	1.1312	36.36*	
	23.95	1.1731			36.44	
34.9	28.00	1.2026	20.58	1.1576	39.11	1.3633
	28.08	1.2014	20.58	1.1591	39.30	1.3690
	27.95	1.2015	20.58	1.1584	39.09*	1.3662
	28.01	1.2018			39.38*	
					39.22	
49.8	33.26	1.2360	26.16	1.2009	41.98	1.3975
	33.00	1.2340	26.23	1.2000	41.99	1.3964
	33.13	1.2350	26.20	1.2004	42.12*	1.3970
					42.06*	
64.7					42.04	
	37.05	1.2627	31.45	1.2432	44.28	1.4071
	36.83	1.2644	31.41	1.2421	44.27	1.4077
	36.94	1.2635	31.43	1.2426	44.72*	1.4074
					44.48*	
79.6					44.44	
	40.36	1.2853	36.87	1.2794		
	40.54	1.2850	36.83	1.2779		
84.7	40.45	1.2854	36.85	1.2786		
			37.96	1.2891		
			38.33	1.2942		
89.6			38.15	1.2916		
94.7			38.08	1.2959		
99.7			38.25	1.2870		
	43.83	1.3148	37.45	1.2928		
	43.72	1.3082	37.55	1.2849		
	43.78	1.3115	37.55	1.2806		
			37.65	1.2861		
			37.47			
			37.53			

\* As oxalate, the rest as ferrocyanide.

*Results of Experiments.*—The values obtained for the solubilities of calcium and potassium ferrocyanide lie on two smooth curves (Fig. 2). The values obtained by Vallance and by Fabria (*loc. cit.*) for the potassium salt, which are plotted on our curve for purposes of comparison, are in good agreement with our measurements except at temperatures above 84°, where Fabria's values are considerably higher. To what extent the divergence is due to his having kept his solutions at these high temperatures for as long as 3 hours we are unable to say, but we have repeatedly noticed that solutions of the calcium salt show green coloration on

cooling, owing presumably to incipient decomposition. The experimental difficulties with the calcium salt solutions at high temperatures were considerable. The solutions had both high viscosity and high density; the former made the rate of flow into the pipette very slow, and also prevented the very small particles of solid salt from settling rapidly. It was almost impossible to prevent the capillary entrance to the pipette from being blocked, and although five determinations were made for the solubility at

FIG. 2.



I. Density of sodium ferrocyanide solutions. II. Density of potassium ferrocyanide solutions. III. Solubility of sodium ferrocyanide. IV. Solubility of potassium ferrocyanide. V. Density of calcium ferrocyanide solutions. VI. Solubility of calcium ferrocyanide.

79.6° these are not given, as they show almost the same value as that obtained at 65°.

As may be seen from the graph, the solubility curve of sodium ferrocyanide shows a sharp break at 81.7°. This transition temperature does not appear to have been observed before, though it is apparently responsible for the reported transition in the curve for the potassium salt of Étard (*loc. cit.*). Work is in progress on the three-component system calcium ferrocyanide-sodium ferrocyanide-water, and the identity of the lower hydrate of the sodium

salt will be investigated. The four points given by Conroy (*loc. cit.*) for the solubility of the sodium salt lie almost exactly on our curve, though, as the number of his determinations was small, the transition point evidently escaped his observation. The density results (Fig. 2) require little comment. No other work appears to have been done on this property of the saturated solutions. The three curves are of the same general form as the corresponding solubility ones. In the case of the sodium salt, the points evidently lie on two curves and are consistent with the transition at  $81.7^{\circ}$  as given by the solubility curve.

*Verification of the Transition Temperature of Sodium Ferrocyanide.*

—The transition point was verified by the two following methods :  
1. *The cooling curve.* On allowing the salt to cool from about  $90^{\circ}$  to  $75^{\circ}$  in a jacketed test-tube carrying a copper stirrer and a sensitive thermometer, arrests were observed, in three experiments, at  $81.0^{\circ}$ ,  $81.2^{\circ}$ ,  $81.3^{\circ}$ , giving a mean value of  $81.2^{\circ}$ .

2. *Dilatometer.* The dilatometer used was of the ordinary form and had a graduated capillary neck about a foot long. The bulb contained the hydrate ( $10\text{H}_2\text{O}$ ) and sufficient paraffin to rise to a convenient level in the capillary when the temperature was in the region of  $81^{\circ}$ . Before the dilatometer was introduced into the thermostat it was heated above  $81^{\circ}$  so as always to have some of the higher-temperature hydrate present to facilitate the change. In all, six experiments were carried out at temperatures ranging from  $80.6^{\circ}$  to  $82.6^{\circ}$ .

At the highest temperature,  $82.6^{\circ}$ , there was a rapid rise of 1 inch in nearly 3 minutes, and at  $81.9^{\circ}$  the level of the oil still rose, although at the rate of only  $\frac{1}{2}$  inch in  $\frac{1}{2}$  hour. In the next three determinations at  $81.2^{\circ}$ ,  $81.3^{\circ}$ , and  $81.3^{\circ}$ , respectively, no change in the oil level could be observed. Finally, at  $80.6^{\circ}$ , there was a fall in the level of  $\frac{1}{2}$  inch in  $\frac{1}{4}$  hour. These experiments show that the change from the higher-temperature hydrate to the  $10\text{H}_2\text{O}$ -hydrate occurs with a volume decrease and vice versa, and that the most probable value of the transition temperature is  $81.5^{\circ}$ . The values obtained by the less accurate methods, namely,  $81.7^{\circ}$  by the solubility, and  $81.2^{\circ}$  by cooling curves, give as a mean value one very close to the most trustworthy value of  $81.5^{\circ}$ .

*Summary.*

1. The solubility of sodium, potassium, and calcium ferrocyanide in water has been determined, together with the density of the saturated solutions.
2. Sodium ferrocyanide has a transition point at  $81.5^{\circ}$ . Neither the potassium nor the calcium salt shows any transition over the

range investigated, the transition point of the potassium salt recorded by Étard being probably due to contamination with sodium ferrocyanide.

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## XII.—*Studies of Valency. Part VII. Surface Polarity and the Reaction of Ethylene and Chlorine—The Effect of the Adsorbed Water Layer.*

By RONALD GEORGE WREYFORD NORRISH and GRIFFITH  
GLYN JONES.

THE reaction between ethylene and bromine which occurs only at the surface of the reaction vessel (Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, 45, 1014) has been shown by one of us to depend greatly on the nature of the surface (Norrish, *J.*, 1923, 123, 3006). The following figures represent the mean bimolecular velocity coefficients found for the surfaces specified in vessels of uniform dimensions: Glass, 0.0506; stearic acid, 0.0864; cetyl alcohol, 0.0266; paraffin wax, 0.0030. The low value for paraffin wax suggested that these figures might be taken as a measure of the polarity of the surfaces and that with an improvement in technique the method might be used as a general measure of surface polarity.

The present research has been undertaken to investigate the effect of moisture on the reactivity of glass and paraffin surfaces and to test a suggestion put forward in the previous paper on ethylene and bromine (*loc. cit.*), that the absolute reactivity of a paraffin surface is vanishingly small.

In these experiments we have substituted chlorine for bromine since it is more easily manipulated than the latter and admits of the pressures of the reactants being increased tenfold. Furthermore, an easier means of experimentation, which gives accurate and reproducible results, has been devised. As was expected, in view of the previous results, the reaction between ethylene and chlorine (in the absence of light) has been found to occur entirely at the surface, and to depend on the nature of the surface in the same way as the reaction of ethylene and bromine already studied. It has further been shown that whilst the rate of reaction at a paraffin wax surface is independent of the presence of water vapour, this is not so for a glass surface, the gases, in the presence of water vapour at 6 mm. pressure, uniting 1.3 times as fast as when they were dried

by phosphoric acid. Further, by taking special precautions to prevent accidental exposure of the glass, it was found possible practically to suspend the reaction in a paraffin vessel, less than 0.1 of the total reactants combining in the course of 12 hours, whilst, in the case of a glass vessel of the same dimensions, the reaction was practically complete in 30–40 minutes. This indicates a reactivity for a paraffin surface some 1200 times smaller than for a glass surface of the same dimensions, whereas the earlier ethylene-bromine experiments indicated a reactivity for paraffin wax only 18 times smaller than that for glass.

FIG. 1.

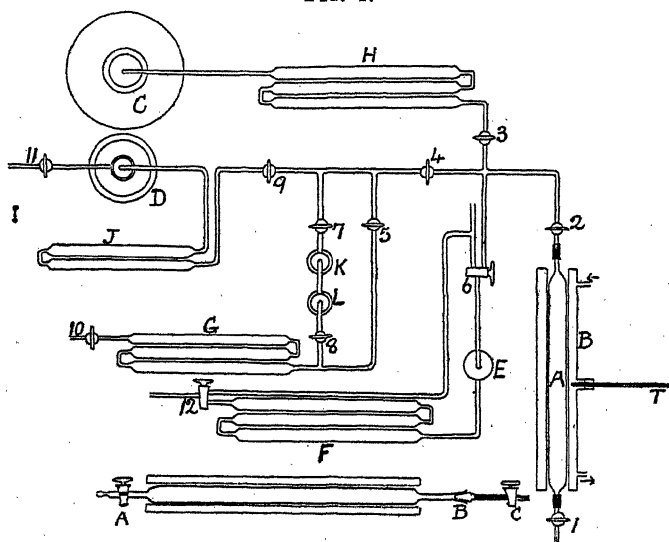


FIG. 2.

### EXPERIMENTAL.

The reaction vessel (Fig. 1, A) consisted of a glass tube 35 cm. long and either 1.3 or 2.7 cm. in diameter. The tube was water-jacketed by an outer metal vessel, B, which served to screen it from light and was kept at constant temperature by a current of water circulated by a pump from a thermostat regulated to  $0.1^\circ$ , the temperature being indicated by a thermometer T. One end of the reaction vessel was connected *via* tap 1 and a long capillary tube to a vertical mercury manometer M; the other end was connected *via* tap 2 to the gas supply and water-pump. As it was necessary frequently to remove the reaction vessel, its connexion with taps 1 and 2 was made at first by paraffined rubber pressure tubing and



later by ground glass joints. The apparatus could be evacuated *via* taps 2, 4, 9, 11, by way of the drying tubes, J, containing phosphoric oxide, and the expansion chamber, D, containing calcium chloride. Dry air could be admitted *via* the drying tubes, G, containing calcium chloride and phosphoric oxide, by way of taps 10, 5, 4, 2. Air saturated with water vapour could be admitted by way of the saturators L and K and taps 10, 8, 7, 4, 2. The saturators were so arranged that the air bubbled through the liquid in L and passed over the surface of the liquid in K. Ethylene was stored in the aspirator, C, and could be expanded into the reaction vessel by way of the calcium chloride-phosphoric oxide drying system, and taps 3 and 2. Dry chlorine was obtained *via* taps 6 and 2 from the chlorine chamber, E, which was kept continually filled by the passage of chlorine from a cylinder, through the phosphoric oxide drying system, F. The technique of the chlorine manipulation was similar to that already described by Norrish and Rideal (J., 1925, 127, 787).

An experimental run was carried out as follows. The vessel A was evacuated as far as possible by the water-pump, and washed out with dry air and re-evacuated several times. Finally air, either dry or moist as required, was admitted to a pressure of about 300 mm. The connecting tubes were evacuated and washed out two or three times with ethylene, and then dry ethylene was admitted to the reaction vessel to a partial pressure of 200 mm. Finally, after the connecting tubes had been washed out as before, dry chlorine was admitted to a partial pressure of 200 mm. Stop-cocks 1 and 2 were kept closed throughout the reaction and readings of the pressure were made at intervals by momentarily putting the mercury manometer into communication with A by opening tap 1; when these precautions were taken, the mercury of the manometer was not affected by the chlorine if this gas was the last to be admitted to the system.

The bimolecular reaction coefficient used as a measure of the reactivity of a given surface was calculated by the formula

$$k = x/a(a - x)t,$$

where  $a$  is the initial pressure of ethylene or chlorine, and  $x$  the fall in pressure of either gas at time  $t$ . The value of  $a$  was fixed at 200 mm., and the value of  $x$  calculated from the fall of pressure in the reaction chamber, account being taken of the fact that the ethylene dichloride is initially formed as a gas and finally separates as a liquid when its saturation vapour pressure is reached. This vapour pressure is 55 mm. at 18°, and 60 mm. at 20° (Rex, *Z. physikal. Chem.*, 1906, 35, 358); hence if  $dp$  represents the pressure fall at time  $t$  at 20°, then, when  $dp < 60$  mm.,  $x = dp$ , and when

$dp > 60$  mm.,  $x = (dp + 60)/2$ . There was, in general, no noticeable change in the value of  $k$  at the moment when liquid ethylene dichloride separated, a fact which proves that the liquid exerts no appreciable catalytic activity in the reaction.

For a reaction which occurs solely at the surface, as in the present case, it may be shown that the reaction coefficient, calculated as above in terms of pressure changes, must be multiplied by the factor  $v/s$ , representing the ratio of volume to surface of the reaction vessel, in order to obtain comparable figures for different-sized vessels. In the present experiments, cylindrical tubes of uniform length were used as the reaction vessels, for which  $v/s \propto d$ , where  $d$  is the diameter of the tube. Thus, by taking the product  $kd$  we obtain comparable figures for surface reactivity. In Tables I and IV examples are given in full of various experiments. The further account of this work will be limited to giving figures for surface reactivity, in Tables II and III, calculated as described above from the mean reaction velocity coefficients.

TABLE I.

Effect of water vapour on the reaction of ethylene and chlorine at a glass surface.

Diameter of tube, 1.30 cm. Temp., 18°.

Experiment "Glass 10."			Experiment "Glass 11."		
$\alpha$ , 200 mm. Water vap. press., 0.			$\alpha$ , 202 mm. Water vap. press., 6.2 mm.		
Time (mins.).	Total pressure fall (mm.).	$k \times 10^4$ .	Time (mins.).	Total pressure fall (mm.).	$k \times 10^4$ .
0	0	—	0	0	—
2	49	8.1	2	69	11.0
4	95	7.5	4	131	10.6
6	129	7.1	6	174	10.8
8	159	7.4	8	204	11.1
10	181.5	7.2	10	224.5	11.0
12	199	7.3	12	239.5	11.1
15	220	7.3	14	251	11.1
18	234	7.2	16	261.5	11.2
21	245.5	7.3	18	267	10.8
25	256.5	7.0	21	276	10.6
30	266.5	6.8	25	284	10.3
Mean 7.3			Mean 10.9		
Surface reactivity ( $kd$ ) =			Surface reactivity ( $kd$ ) =		
$9.5 \times 10^{-4}$ .			$14.2 \times 10^{-4}$ .		

From the data of Table II, which are given in the order of experimentation, it will be seen that the surface reactivity,  $kd$ , is uniformly higher for moist gases than for dry, the mean value, calculated from the recorded figures, being  $11.3 \times 10^{-4}$  for dry gases and  $14.8 \times 10^{-4}$  for moist gases, while the ranges of surface reactivity in the two cases do not overlap. Thus the presence of about 6 mm. of

TABLE II.

Effect of water vapour on the reaction of ethylene and chlorine at a glass surface—collected data.

Diameter of tube, 1.30 cm.

Expt. No.	Temp.	Water vapour pressure.	Bimolec. reaction coeff. $k \times 10^4$ .	Surface reactivity. $kd \times 10^4$ .
2	18°	0	8.2	10.7
4	19	0	7.9	10.3
5	18	6.0	11.0	14.3
6	19	6.6	11.7	15.2
7	19	0	9.6	12.5
9	16	5.1	11.6	15.1
10	18	0	7.3	9.5
11	18	6.2	10.9	14.2
12	18	5.5	12.0	15.6
13	18	0	10.0	13.0
14	18	0	9.0	11.7
15	18	0	8.9	11.6
16	18	6.2	11.0	14.3

TABLE III.

Effect of water vapour on the reaction of ethylene and chlorine in a paraffin wax tube (rubber connexions).

Temperature, 20°.

Tube No.	Diam. of tube (cm.).	Press. of water vapour (mm. Hg).	Vel. coeff. $k \times 10^4$ .	Surface reactivity. $kd \times 10^4$ .
1	1.3	6	0.74	0.97
		0	0.65	0.85
		0	0.71	0.92
		0	0.17	0.45
2	2.7	6	0.17	0.47
		0	0.13	0.37
3	2.7	0	0.13	0.37
		6	0.12	0.33

water vapour in the gas phase increases the reactivity of a glass surface by about 30%.

It will be seen from the data for a given tube that the presence of water vapour has no measurable effect upon the reactivity of a paraffin wax surface. Further, the velocity coefficient does not vary in inverse ratio to the diameter of the tube as it would if the reactivities of the paraffin surfaces were uniform, and it was therefore thought that the measured reactivity was to be ascribed in part at least to the presence of the rubber connexions. In order to measure the absolute reactivity of a paraffin wax surface, the rubber connexions were replaced by ground glass joints, which together with the stop-cocks were lubricated with a grease made by melting together "nujol" and paraffin wax. The tube was constructed as shown in Fig. 2; the gases being introduced through the end A, and the end B being attached to the manometer. The paraffin

wax was introduced molten into the tube, and allowed to cool with constant agitation under a vacuum, the process usually having to be repeated several times before a uniform coat was obtained. The tube fitting the ground glass joint, and communicating with the manometer, was paraffined carefully on both sides of the tap C. Great difficulty was experienced in preparing satisfactory tubes; in most cases there was some small surface of glass incompletely protected which enabled a slow reaction to proceed. After many trials, however, two cases of very low reactivity were obtained. In the better of the two, with both reactants at *ca.* 200 mm. pressure, less than 0.1 of the total reaction had occurred after 12 hours. The experimental figures are in Table IV.

TABLE IV.

Tube dimensions : length, 35 cm.; diameter, 1.3 cm.

Experiment i. Temp., 20.4°. Pressure of $C_2H_4$ , 197 mm. Press. of $Cl_2$ , 200 mm.			Experiment ii. Temp. 20.0°. Pressure of $C_2H_4$ , 220 mm. Pressure of $Cl_2$ , 182 mm.		
Time (mins.).	Pressure decrease (mm.).	Bimolec. coeff. $\times 10^6$ .	Time (mins.)	Pressure decrease (mm.).	Bimolec. coeff. $\times 10^6$ .
0	0	—	0	0	—
16.5	3.5	5.5	124	3.9	0.88
46	8.2	4.8	227	5.5	0.64
146	18.0	3.5	358	7.0	0.53
194	21.0	3.2	449	11.0	0.65
226	25.0	3.3	825	20.0	0.60
339	35.6	3.3	955	24.4	0.72
455	45.4	3.3	1096	32.5	0.89
525	52.0	3.7	1182	42.0	0.95

To ascertain that the gases remained unreacted in the tube, in experiment ii, they were slowly withdrawn, after 20 hours, through potassium iodide solution. The quantity of unreacted chlorine (estimated by the amount of iodine set free, equiv. to 7.20 c.c. of 0.1*N*- $Na_2S_2O_3$ ) was in satisfactory agreement (5%) with that (7.56 c.c.) calculated from the known volume of the tube (48 c.c.) and the observed pressure changes.

The reactivity of the tube in experiment ii was much lower than that in experiment i, a fact which suggests that this residual activity was entirely due to the accidental exposure of glass surface.

*Reactivity of a Stearic Acid Surface.*—As data for comparison with the experimental results of the ethylene-bromine reaction (*loc. cit.*), figures were obtained for the reactivity of a stearic acid surface, a tube of 2.7 cm. diameter being used. The tube was coated with stearic acid under the conditions described above for paraffin wax and the initial pressure of each reactant was fixed at 200 mm. The

constancy of the velocity coefficients was good, there being no variation from the mean values greater than 5%. In two experiments the mean values were  $4.52 \times 10^{-4}$  and  $4.20 \times 10^{-4}$ .

In Table V is a comparison of the relative surface reactivities measured by the ethylene-chlorine and by the ethylene-bromine reactions. These are referred to the reactivity of glass, taken as unity, by computing the ratios of the reactivities of the given surfaces to that of glass, the reactivity being measured, in the way described above, as the product of the bimolecular reaction coefficient and the diameter of the tube.

TABLE V.

Comparative surface reactivities by two methods.

Surface	Glass; gas dry.	Glass; gas wet.	Stearic acid; gas dry.	Paraffin wax with rubber.	Paraffin wax, optimum.
$C_2H_4-Br_2$	1.0	—	1.7	0.06	—
$C_2H_4-Cl_2$	1.0	1.3	1.06	0.076	0.0008

It will be seen that the results of the earlier work have been confirmed, while the prediction that the non-polar surface of paraffin wax is entirely unreactive has been practically demonstrated.

The results described above, when considered with reference to the adsorbed water layer which is known to exist at the surface of glass, would seem to have an important bearing on any explanation of the suspension of reactions by extreme drying. The adsorbed water layer, under "dry" conditions, is probably but one molecule thick, but tends to pile up as the vapour pressure is increased towards saturation point (McHaffie and Lenher, J., 1925, 127, 1559). Hence, if we assume that the water layer is the polar catalyst in the case of the glass surfaces, we can explain the increased reactivity of moist gases as due to the more complete saturation of the surface water film. When the surface is covered with paraffin wax, it seems reasonable to assume that the water layer cannot form, in agreement with the fact that water shows no tendency to wet paraffin wax. There is thus no reaction, either with dry or with wet gases, a fact which shows also that no volume reaction sets in, in the presence of water vapour. It seems highly probable that we are here imitating the effects of Baker: by the extreme drying of his systems we may suppose that he was removing the water from the walls, while by using walls composed of a substance in which water cannot condense we achieve the same result, even in the presence of moist gases. Finally, if a polar group such as carboxyl or hydroxyl be introduced into the paraffin molecule, we can imitate the effect of the water layer on glass; thus with walls composed of stearic acid, or cetyl alcohol, the surface becomes once more reactive.

If we inquire further as to the mechanism of the present reaction, there is little evidence to guide us. It seems probable, however, that the presence of water on the surface might cause a greater modification of the dielectric constant in the immediate vicinity of the surface than can be brought about by a single molecule in the ternary complex  $[A \cdot H_2O \cdot B]$ , so that the whole reaction takes place through the medium of the adsorption layer, even in the presence of water vapour. It seems significant also that all the polar catalysts so far obtained contain oxygen, and we might regard their function as the formation of a complex with the chlorine molecule, through the medium of quadrivalent oxygen (e.g.,  $\begin{array}{c} H \\ | \\ H > O < \begin{array}{c} Cl \\ | \end{array} \end{array}$ ) which, under the influence of the surface forces, is more dissociable than the chlorine molecule itself.

#### *Summary.*

A study has been made of the reaction between ethylene and chlorine, each at an initial partial pressure of 200 mm., at the surface of glass, paraffin wax, and stearic acid. By taking special precautions, a paraffin wax-surface was prepared showing a reactivity some 1200 times smaller than that of glass and about 70 times less than that previously found for a paraffin wax surface in the experiments on the union of ethylene and bromine. It has been shown that water vapour present at a partial pressure of 6 mm. increases the reactivity of the glass surface by 30%, whilst it has no effect on the paraffin wax surface. These results are discussed from the point of view of surface polarity and in the light of our knowledge of the adsorbed water film existing at the surface of many solid substances.

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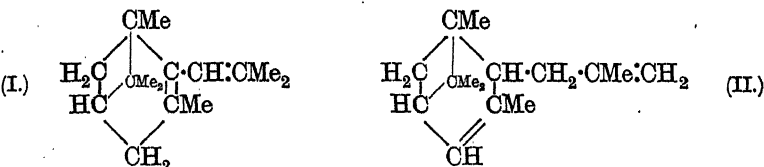
[Received, November 26th, 1925.]

### XIII.—*The Chemistry of the Caryophyllene Series.* *Part I.*

By GEORGE GERALD HENDERSON, JOHN MONTEATH ROBERTSON,  
and (in part) CARL ALOYSIUS KERR.

$\beta$ -CARYOPHYLLENE belongs to the dicyclic series of sesquiterpenes, but as no naphthalene or benzenoid derivative can be obtained from it by the sulphur method (Ruzicka and Stoll, *Helv. Chim. Acta*, 1923, 6, 854), it cannot be assigned to either of the known cadinene or eudesmol types. Its structure is therefore largely a matter of conjecture, although Semmler and Mayer (*Ber.*, 1911, 44, 3657) consider that it consists of a mixture of two forms, for which, from

a study of the ozonide products, they have advanced formulæ I and II. The existence of the bridge ring system is, however, based upon the supposed identity of caryophyllenic acid with *cis*-2 : 2 : 3-trimethylcyclobutane-1 : 3-dicarboxylic acid, and until this is definitely established these formulæ must be regarded as tentative.



Wallach and Walker (*Annalen*, 1892, **271**, 285) showed that caryophyllene forms a crystalline hydrate known as caryophyllene alcohol,  $C_{15}H_{25}\cdot OH$ , upon hydration with a mixture of sulphuric and acetic acids. The properties of this alcohol and in particular its relation to the hydrocarbon have not previously been fully examined. As there is some evidence that certain of its derivatives possess a different molecular configuration from that assigned to  $\beta$ -caryophyllene, experiments were carried out with a view to obtain more information in this connexion.

The alcohol prepared by the hydration method was found to be remarkably stable in certain respects. Thus, after heating with hydrogen peroxide for 52 hours, practically the whole of the alcohol was recovered unchanged. On treatment with permanganate the alcohol was again recovered unchanged. Towards bromine in chloroform solution it behaved as a fully saturated substance.

All dicyclic sesquiterpene alcohols of the formula  $C_{15}H_{25}\cdot OH$  are unsaturated, uniting additively with bromine and being readily oxidised. It is evident that caryophyllene alcohol does not belong to this class, and therefore cannot be regarded as a direct hydrate of the hydrocarbon, as previously supposed. Apparently the hydrating agents have induced ring closure with the formation of a new tricyclic structure. Confirmation of this view is found in the fact that the alcohol can be formed through the agency of formic acid, which is a well-known means of effecting ring closure in the sesquiterpenes (Robertson, Kerr, and Henderson, J., 1925, **127**, 1944). Moreover, it has long been known that caryophyllene alcohol upon dehydration yields a hydrocarbon, clovene, which is not identical with caryophyllene, but which appears to be tricyclic from its physical properties (Wallach and Walker, *loc. cit.*).

Although it is not feasible to determine the molecular refractivity of caryophyllene alcohol directly owing to its high melting point. (compare Semmler, *Ber.*, 1903, **36**, 1037), it appeared probable that the necessary information might be obtained from the physical

properties of certain of its esters, which were prepared in the course of this work. The following figures were therefore determined for the formate and the acetate, and they clearly indicate the tricyclic nature of the caryophyllene radical.

Ester.	<i>t.</i>	$d_4^{20}$	$n_D^{20}$	Found.	[ $R_L$ ] <sub>D</sub> .		
					Calc. for C <sub>15</sub> H <sub>25</sub> -R. Tricyclic.	Typical * C <sub>15</sub> H <sub>25</sub> -R. Dicyclic.	Calc. for C <sub>15</sub> H <sub>25</sub> -R. Dicyclic.
Formate, C <sub>15</sub> H <sub>25</sub> O <sub>2</sub> †	7°	1.024	1.4998	71.78	71.02	—	72.75
Acetate, C <sub>17</sub> H <sub>23</sub> O <sub>2</sub> †	17°	1.003	1.4919	76.37	75.64	78.13	77.37

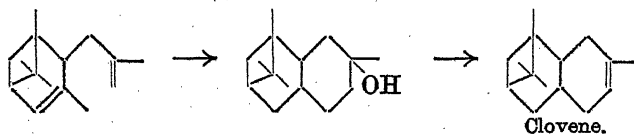
\* Semmler and Jonas, *Ber.*, 1914, 47, 2068, 2072.

† We wish to take this opportunity of correcting the density for the formate previously given (J., 1925, 127, 1945), where  $d_4^{20}$  1.22 should be  $d_4^{20}$  1.024.

‡ Determined on the super-cooled liquid.

It will be observed that the exaltation found in the case of the caryophyllene derivatives is not greater than the corresponding divergence for a typical dicyclic member.

It is noteworthy that the limonene form (II) of active caryophyllene could readily adapt itself to such ring formation as is indicated by the above results. The course of the reaction and the dehydration of the alcohol to clovene may therefore be represented by the following scheme :



In addition to caryophyllene alcohol, Wallach's hydration method gives rise to a liquid product. We find this substance to consist of an unsaturated hydrocarbon, C<sub>15</sub>H<sub>24</sub>, b. p. 110–114°/9 mm.,  $d_4^{20}$  0.9263,  $n_D^{20}$  1.5010,  $[\alpha]_D^{25}$  –19.56°, which evidently differs from  $\beta$ -caryophyllene and is perhaps identical with the tricyclic caryophyllene obtained from the dihydrochloride by the quinoline method (Semmler and Mayer, *Ber.*, 1910, 43, 3451) which had b. p. 122–123°/13 mm.,  $d_4^{20}$  0.927,  $n_D^{20}$  1.50246,  $[\alpha]_D^{25}$  –57°. Clovene, also regarded as tricyclic, has closely similar properties. The possible identity of these three substances is under examination.

Our experiments were next directed towards the synthesis of hydroxyl derivatives from caryophyllene corresponding to the dicyclic structure of the hydrocarbon, since it has been shown that Wallach and Walker's hydration method leads to ring closure. From caryophyllene dihydrochloride by the action of silver acetate in glacial acetic acid solution we obtained products which upon hydrolysis yielded an unsaturated alcohol, C<sub>15</sub>H<sub>25</sub>·OH, a saturated glycol, C<sub>15</sub>H<sub>26</sub>(OH)<sub>2</sub>, and some regenerated hydrocarbon. The



alcohol,  $C_{15}H_{25}\cdot OH$ , which may be termed *caryophyllol*, has properties corresponding closely to those of a dicyclic sesquiterpene alcohol. Although it reacts with sodium, no ester has yet been obtained by any of the usual methods, which indicates that the alcohol is tertiary. By the action of a chloroform solution of bromine in the cold it is converted into a rather unstable *dibromide*,  $C_{15}H_{26}OBr_2$ .

The compound  $C_{15}H_{26}(OH)_2$  is quite a stable substance, and is probably a glycol with both hydroxyl groups attached to tertiary carbon atoms. It possesses properties closely similar to those of cadinene glycol (Henderson and Robertson, J., 1924, 125, 1992). The fact that the hydrocarbon product of the reaction gives a good yield of caryophyllene dihydrochloride on treatment with hydrogen chloride indicates that these hydroxyl derivatives also retain the dicyclic caryophyllene structure.

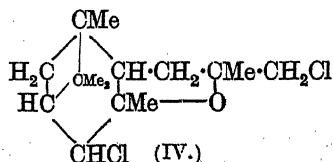
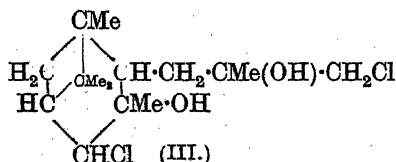
Wallach and Walker (*loc. cit.*) found that caryophyllene alcohol gives a series of halogen derivatives, of which the chloride,  $C_{15}H_{25}Cl$ , can be readily obtained. We have found that this compound also, as was to be expected from the above results, behaves as a fully saturated substance like the alcohol, and therefore must also be regarded as being tricyclic. It thus becomes of interest to enquire whether hydrogen chloride can be eliminated from this compound by any of the usual methods, because if this proved to be the case, a new type of tricyclic sesquiterpene would be expected, of which the above-mentioned compound would be the hydrochloride.

We have found that this chloride is much more stable than the known hydrochlorides of the sesquiterpene series. Even after prolonged heating in a concentrated alcoholic solution of sodium ethoxide, or with quinoline, practically all the compound was recovered unchanged. On treatment with sodium acetate in glacial acetic acid solution, however, chlorine was removed from the molecule, but the product of the reaction in this case proved to be the *acetate* of caryophyllene alcohol,  $C_{15}H_{25}\cdot OAc$ . Wallach and Tuttle (*Annalen*, 1894, 279, 393) mention a caryophyllene acetate, but as no melting point or other data are given, it is impossible to state whether the compound we have obtained is similar to theirs.

Since hypochlorous acid has proved of service in investigating the simpler terpenes (compare Slawinski, *Ber.*, 1899, 32, 2064; Henderson and Marsh, J., 1921, 119, 1492; Henderson and Kerr, J., 1924, 125, 102), we examined the action of this reagent on  $\beta$ -caryophyllene. In this case, however, instead of using a dilute aqueous solution of the acid we adopted Detoeuf's method of preparing chlorohydrins (*Bull. Soc. chim.*, 1922, 31, 102, 169, 176)

through the agency of chlorocarbamide, which in acid solution undergoes hydrolysis with formation of carbamide and hypochlorous acid. In order to regulate the reaction and to diminish the rate of hydrolysis of the chlorocarbamide, the caryophyllene was dissolved in 4—5 times its bulk of acetone. The first product of the reaction was not obtained in a pure state, but appeared to be a *dichlorohydrin* of caryophyllene,  $C_{15}H_{24}Cl_2(OH)_2$ . On treatment with acetic anhydride it yielded a small quantity of a *monoacetate*, but also in an impure state. When distilled at 1 mm. pressure, it was converted into a *saturated compound* of the formula  $C_{15}H_{24}OCl_2$ . This substance, a colourless liquid, appears to be the anhydride of the dichlorohydrin. The chlorine in this compound is not easily replaced, and oxidation with hydrogen peroxide yielded no definite product except some succinic acid.

If  $\beta$ -caryophyllene has the constitution (II) given above, the constitution of the dichlorohydrin may be represented by the formula (III) and that of the anhydride by (IV).



It is true that the supposed anhydride does not undergo hydration to the corresponding glycol on treatment with dilute sulphuric acid, but Franke and Lieben (*Monatsh.*, 1914, **35**, 431) have shown that the anhydrides of 1:4- and 1:5-glycols are quite stable in this respect.

#### EXPERIMENTAL.

*Preparation and Properties of Caryophyllene Alcohol.*—The  $\beta$ -caryophyllene used in the following experiments was purified by fractional distillation (compare Robertson, Kerr, and Henderson, *loc. cit.*). To 1 litre of acetic acid containing 12 c.c. of sulphuric acid and 40 c.c. of water, 150 g. of caryophyllene were added and the whole was maintained at 80—100° for 30 hours. The product was steam distilled. At first acetic acid and an oil passed over, then the solid alcohol slowly distilled. After crystallisation from light petroleum at a low temperature it melted at 94—96° (yield, about 30%).

The liquid product of the hydration was collected by means of light petroleum and dried. On removing the solvent and allowing the product to remain 24 hours at 0°, a further quantity of the alcohol separated and was removed. The resulting oil was distilled under diminished pressure and the main fraction was finally redis-

tilled over sodium in a vacuum. The product consisted of a colourless oil with a pleasant odour which had b. p. 110—114°/9 mm.,  $n_D^{20}$  1.5010,  $d_4^{20}$  0.9263,  $[\alpha]_D^{25}$  -19.56°.  $[R_L]_D$  found, 64.8; calc. for a tricyclic sesquiterpene, 64.4 (Found: C, 87.7; H, 11.7.  $C_{15}H_{24}$  requires C, 88.2; H, 11.8%). This substance was unsaturated towards bromine.

Caryophyllene alcohol (50 g.) in glacial acetic acid (200 c.c.) and 30% hydrogen peroxide (55 c.c.) were heated together at 50—55° for 52 hours. The solution was then neutralised, when practically the whole of the caryophyllene alcohol was recovered unchanged. M. p. 94°. On standing in the cold with 1% permanganate the latter was not decolorised, and the alcohol was recovered unchanged. When the alcohol was gradually treated with bromine, both in chloroform solution at room temperature, no absorption or substitution could be detected.

*Preparation and Properties of Other Hydroxyl Derivatives of Caryophyllene.*—The dihydrochloride of caryophyllene was prepared by gradually treating caryophyllene (100 g.) in anhydrous ether (100 c.c.) with dry hydrogen chloride, the temperature of the reaction being kept at 0°. After remaining a further 24 hours at 0°, the ether was removed by passing a current of dry air over the surface of the liquid. On reducing the temperature to -20°, practically the whole of the liquid crystallised. Recrystallised from ethyl acetate, caryophyllene dihydrochloride had m. p. 69°,  $[\alpha]_D^{25}$  +67° in 2.5% ethyl-alcoholic solution. Failure to observe the conditions stated, in particular with regard to temperature, results in a greatly diminished yield of the dihydrochloride.

A solution of caryophyllene dihydrochloride (50 g.) in glacial acetic acid (250 g.) was gradually treated with silver acetate (70 g.). The mixture was shaken for 2 to 3 hours at room temperature, and the reaction completed by gently warming on the water-bath. On cooling, the silver chloride was filtered off, and the acetic acid neutralised with sodium carbonate. The resulting product, consisting principally of acetates, was collected by means of ether and hydrolysed by warming with dilute methyl-alcoholic potash for  $\frac{1}{2}$  hour. After the alcohol had been distilled off, the product was rendered neutral with carbon dioxide and steam distilled. The portion volatile in steam was collected with ether, dried over anhydrous sodium sulphate, and distilled under reduced pressure. After several distillations, three principal fractions were obtained: (a) b. p. 122—130°/10 mm., (b) b. p. 130—140°/10 mm., and (c) b. p. 140—150°/10 mm. The fraction (a) consisted of regenerated caryophyllene. When treated with hydrogen chloride in the manner described above, an almost theoretical yield of the dihydrochloride,

m. p. 69°, was obtained. The fraction (c), which represented about 20% of the product, on further purification had b. p. 142–150°/10 mm.,  $d_4^{20}$  0.9632,  $n_D^{20}$  1.5015;  $[R_L]_D$  found, 68.03; calc. for a dicyclic sesquiterpene alcohol, 68.12 (Found: C, 80.6; H, 11.2.  $C_{15}H_{26}O$  requires C, 81.1; H, 11.7%). This substance gave no solid derivative when treated in the usual manner with phthalic anhydride, or with phenylcarbimide, and therefore appears to be a tertiary alcohol. On boiling with acetic anhydride, dehydration occurred yielding a hydrocarbon. The alcohol is unsaturated towards bromine and alkaline permanganate. When slowly treated with bromine at 0°, both in chloroform solution, absorption occurred but no substitution was detected. The chloroform was removed under reduced pressure, leaving a colourless, oily dibromide (Found: Br, 40.1.  $C_{15}H_{26}OBr_2$  requires Br, 41.8%) which slowly decomposed on exposure to light. The fraction (b) consisted of a mixture of the above alcohol and the hydrocarbon. A small higher-boiling fraction was also obtained, containing a higher percentage of oxygen, which probably consists of a mixture of the above alcohol with a small amount of the glycol referred to below.

The residue from the steam distillation contained a thick brown oil, which was repeatedly extracted with ether and dried. On removing the ether, most of this substance crystallised and by the addition of a small amount of light petroleum the remainder was deposited in minute, white needles. The substance was recrystallised from ether as a flocculent mass of minute needles, m. p. 173° (yield 3%). The composition corresponds with that of caryophyllene glycol,  $C_{15}H_{26}(OH)_2$  (Found: C, 74.5; H, 11.7.  $C_{15}H_{28}O_2$  requires C, 75.0; H, 11.7%). The substance is very soluble in alcohol, slightly soluble in ether, and almost insoluble in light petroleum. It does not decolorise bromine or alkaline permanganate solution.

*Reactions of Chlorodihydrocaryophyllene.*—The chloro-compound,  $C_{15}H_{25}Cl$ , was prepared by the action of phosphorus pentachloride on the alcohol (Wallach and Walker, *loc. cit.*) and purified by crystallisation from light petroleum. M. p. 63° (Found: Cl, 14.9. Calc., Cl, 14.8%). The yield was almost theoretical.

A portion was refluxed at 100° with a concentrated solution of sodium ethoxide for 12 hours. No action took place and the chloride was recovered unchanged. Another portion was heated at 210° in quinoline solution for 3 hours, but again the compound was recovered unchanged. A third portion (20 g.) was dissolved in glacial acetic acid (150 c.c.), and anhydrous sodium acetate (19 g.) gradually added. The solution was boiled for 3 hours. After 1 hour, sodium chloride began to be deposited. On cooling, the product was diluted with water and extracted with light

petroleum. After removing the solvent from the dried extracts, the product was distilled under reduced pressure, when a colourless oil was obtained, b. p. 149—152°/10 mm., which was saturated towards bromine. When mixed with light petroleum and cooled to -20°, a solid mass of small, white crystals separated, which on purification melted at 40°. The yield was nearly theoretical. This substance is fairly soluble in alcohol and in petroleum. Acid ethyl-alcoholic hydrolysis yielded ethyl acetate, and by hydrolysis with methyl-alcoholic potash a theoretical yield of caryophyllene alcohol, m. p. and mixed m. p. 95°, was obtained. The substance is therefore caryophyllene acetate,  $C_{15}H_{25}O \cdot CO \cdot CH_3$  (Found: C, 76.8; H, 10.6.  $C_{17}H_{28}O_2$  requires C, 77.2; H, 10.6%).

*The Action of Hypochlorous Acid on  $\beta$ -Caryophyllene.*—A solution of 108 g. of chlorocarbamide (2 mols.) in 300 c.c. of water was added slowly to a cooled solution of 120 c.c. of  $\beta$ -caryophyllene (1 mol.) and 10 c.c. of acetic acid in about 500 c.c. of acetone, and the mixture shaken for several hours until all the hypochlorous acid had disappeared. The acetone was then distilled off, the residual liquid extracted with ether, and the extract dried and distilled. The product, which presumably was the dichlorohydrin of  $\beta$ -caryophyllene,  $C_{15}H_{24}(OH)_2Cl_2$ , was a yellow, oily liquid, which could not be obtained in crystalline form, was not volatile in a current of steam, and could not be distilled without partial decomposition. The compound did not give a semicarbazone nor a nitrobenzoate, but when a portion was warmed with acetic anhydride (2 mols.) after addition of a drop of sulphuric acid reaction took place quickly. The product was extracted and after repeated distillation under diminished pressure yielded a colourless liquid, b. p. 190—200° of which the composition approximated to that of a monoacetate of the dichlorohydrin (Found: C, 57.1; H, 6.9; Cl, 19.9.  $C_{17}H_{28}O_3Cl_2$  requires C, 58.1; H, 7.1; Cl, 20.2%). The supposed dichlorohydrin distilled at 1 mm. with little decomposition. Repeated fractionation finally yielded a colourless liquid, b. p. 125—140°/1 mm., which was essentially the anhydride of the dichlorohydrin (Found: C, 62.3; H, 7.9; Cl, 23.4.  $C_{15}H_{24}OCl_2$  requires C, 61.8; H, 8.3; Cl, 24.3%).

This compound is saturated towards both bromine and potassium permanganate. It does not react with *p*-nitrobenzoyl chloride, with semicarbazide acetate, or with ammoniacal silver nitrate. It is not attacked by boiling aqueous 2% sulphuric acid or by dilute aqueous potassium hydroxide, but when heated with an aqueous alcoholic solution of the last reagent yielded an oily liquid which contained only a trace of chlorine, was unsaturated, and did not give the reactions of an alcohol.

Attempts to replace the chlorine in this compound by hydrogen were not successful. Addition of successive quantities of sodium amalgam to an alcoholic solution containing a trace of water resulted in the production of a yellow, oily liquid, which distilled for the greater part at  $120\text{--}130^\circ/1\text{ mm.}$ , and still contained 14.20% of chlorine. Thus by this treatment approximately one atom of Cl was replaced ( $\text{C}_{15}\text{H}_{25}\text{OCl}$  requires Cl, 13.8%). Prolonged heating of the compound with zinc dust and alcohol failed to yield a substance free from chlorine.

On oxidation with 30% hydrogen peroxide in glacial acetic acid solution the chloroanhydride yielded a small quantity of a viscous neutral product, some succinic acid, and another acid, in the form of a brown oily liquid, which has not been identified.

We are grateful to the Carnegie Trust for the award of grants which assisted us to prosecute this work.

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#### XIV.—*The Density of Boric Oxide Glass and the Suspected Variation in the Atomic Weight of Boron.*

By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON,  
and GEORGE EDWARD STEPHENSON.

THROUGH the courtesy of Messrs. Borax Consolidated, Ltd., the authors, in 1922, were in possession of several parcels of boron minerals obtained from various parts of the world and containing a high percentage of boron. At that time an attempt was made to compare the atomic weights of the several specimens of boron contained in these minerals by preparing from each a specimen of boric acid, purifying these specimens by rigorous fractional crystallisation, and determining the density at  $25.00^\circ \pm 0.02^\circ$  of their aqueous solutions saturated at that temperature. The accuracy of the results as measured by their reproducibility fell short, however, of that necessary to give trustworthy evidence of any difference in atomic weight and this method of attack was abandoned.

Thereafter three of the samples of boron were used for determinations of the atomic weight by measurement of the ratio  $\text{BCl}_3 : 3\text{Ag}$  which have already been reported (J., 1925, 127, 700). These determinations gave evidence of an appreciable variation in atomic weight among the three samples. Therefore, as sufficient of all the original mineral samples was still available, a fresh attempt was made to obtain a comparative estimate of the atomic weights by deter-

mining the densities of samples of a solid boron compound prepared from the several sources. Of the available compounds, boric oxide glass appeared to be the most suitable; boric acid is easily prepared from the minerals, its low solubility in cold water renders its recrystallisation an excellent method of purification and it readily dehydrates to yield boric oxide glass, which, because of its chemical stability and transparent glassy character, seemed to be especially well suited to precise density determinations.

Although much attention has been given to the improvement of the specific gravity bottle (see, *e.g.*, Berkeley, J., 1907, 90, 56; Baxter, J. *Amer. Chem. Soc.*, 1908, 30, 46; Johnson and Adams, *ibid.*, 1912, 34, 563), it is difficult to attain high accuracy in the determination of the density of solids by displacement methods. Moreover, as boric oxide is extremely hygroscopic, being in fact coated with an opalescent film of hydrated oxide in less than one minute when exposed to air of ordinary humidity, it is clear that the use of any form of specific gravity bottle for the determination of its density is attended by very serious difficulty. Therefore it was decided to use a modification of the flotation method suggested by Andreae (*Z. physikal. Chem.*, 1911, 76, 491). Beads of pure boric oxide glass prepared from each of six sources, with all precautions to exclude traces of moisture, were sealed up in tubes containing the same mixture of dry, inert organic liquids of suitable density; then careful observations were made of the *temperature* of flotation of the beads of each sample. Separate determinations of the density and thermal expansion of the liquid mixture enabled the actual densities of the boric oxide samples to be calculated. Thence, using the ascertained atomic weight of the boron in one sample as a standard, it was possible, assuming identity of atomic volume for all specimens of boron, to calculate the atomic weights of the specimens of boron in the remaining samples.

#### EXPERIMENTAL.

*Preparation of Beads of Pure Anhydrous Boric Oxide.*—The sources of the various samples were:

- No. 1. Calcined borate of lime; Ascotan, Chile.
- No. 2. Calcined colemanite; Death Valley, California, U.S.A.
- No. 3. Borate of lime; the Argentine.
- No. 4. Borate of lime; Peru.
- No. 5. Boracite; Sultan Tchair, Asia Minor.
- No. 6. Crude boric acid; Volterra, Italy.

Samples 1 to 5 were separately treated as follows: 200 g. of mineral were dissolved as far as possible in hot 10% hydrochloric

acid, the solution was filtered hot, cooled quickly, and the precipitated boric acid was removed by filtration. The acid was twice recrystallised from pure water, the product was fused in platinum and then dissolved in pure hot water and allowed to crystallise. From this stage all the samples of boric acid, including No. 6, were twice recrystallised from pure water and each batch of crystals was tested for purity.

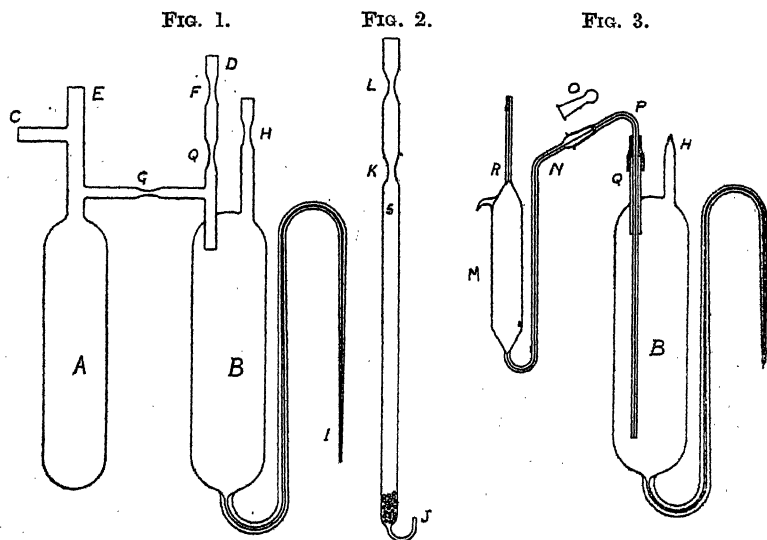
Owing, presumably, to the insolubility of calcium borate and the comparative insensitivity of available tests for calcium, no trace of that metal could be detected in the boric acid even at an early stage of the purification, but sulphate and chloride were then present in detectable amounts. Therefore the progress of purification in the later crystallisations was followed by tests for sulphate and chloride, and the apparent absence of these radicals in the final main crops of boric acid and in the mother-liquors whence these had come was taken as an indication of high general purity. The purified boric acid was stored in clean stoppered bottles, capped to exclude dust.

In the preparation of beads 10 g. of each sample were fused for 4—5 hours in a *suitable* covered platinum crucible heated at about 900° in an electric muffle furnace. The term *suitable* is stressed because it was only after several trials that a platinum crucible was found from which iron was not leached by the melt. Even after this drastic treatment, boric oxide still contains water, presumably because the high viscosity of the melt hinders its escape, and in order to dehydrate the material completely and prepare suitable individual samples for flotation, the crucible was again heated over a Méker burner and a quantity of the fused oxide was collected on a platinum wire. This was heated in a hot bunsen flame for 1 minute and if it then showed no sign of bubbles—a clear indication of the complete absence of water—it was allowed to drop from the wire directly into a clean cold platinum basin, which had been previously heated to redness and then rested in a desiccator over phosphoric oxide, the lid of the desiccator being raised for the minimum time. When bubbles appeared in a bead, the material was rejected, as it was found that such beads could be almost completely volatilised before losing their vesicular structure. The beads were about 3 mm. in diameter and from 30—35 were prepared from each sample. A number of test beads examined under the microscope were isotropic, contained no visible bubbles and, between crossed Nicols, appeared free from strain.

*Preparation of the Flotation Liquid.*—No single liquid of suitable chemical nature having the required density could be found, so a **binary mixture** was used. It appeared that the constituents of this mixture should be chemically stable and non-reactive, should be



capable of being thoroughly dried by means of phosphoric oxide, should have densities slightly below and above 1.8, should have closely similar and preferably rather high boiling points and fairly low viscosities. The requirements of the case were met by a mixture of pentachloroethane (b. p.  $161.7^{\circ}$ ,  $D$  1.693) and trimethylene dibromide (b. p.  $165.0^{\circ}$ ,  $D$  1.987) containing 61.07% by volume of the former liquid. Both liquids were obtained from Messrs. British Drug Houses, Ltd.; and were further purified by fractional distillation, about 20% being rejected as head and tail fractions. The main fraction of pentachloroethane was collected between  $160^{\circ}$  and  $162.5^{\circ}$  at 762.6 mm. and that of trimethylene dibromide between  $164.0^{\circ}$  and  $167.0^{\circ}$  at 762.6 mm.



About 120 c.c. of the mixture were left in contact with phosphoric oxide for 24 hours. Slight decomposition and darkening occurred, probably owing to slight conversion of trimethylene dibromide into propylene dibromide (b. p.  $141.7^{\circ}$ ,  $D$  1.9), but the method of experiment ensured that any change in the density or volatility of the mixture thus produced would have no effect on the density found for boric oxide.

The apparatus used for the final purification and preservation of the flotation mixture is shown in Fig. 1. Both it and the other apparatus to be described later were constructed throughout of "Durosil" glass and before use were soaked in a solution of chromic acid in strong nitric acid, washed very thoroughly with pure water, dried in an air-oven at  $150^{\circ}$ , and finally swept out for some time

with a slow stream of air which had been cleaned by bubbling through concentrated aqueous potash and dried by passage over solid caustic potash and phosphoric oxide. The tubes at H and I being temporarily sealed by fusion, a stream of dry air was passed in at C and out through a phosphoric oxide guard-tube on D, and the liquid mixture was introduced through E into the vessel A: tubes E and C were then sealed. A was cooled with ice and the apparatus was evacuated by a Gaede pump through D, which was finally sealed off at the constriction F. At this stage the liquid was almost completely distilled from A to B. Then both A and B were cooled with ice, dry air was slowly admitted at C, and the vessel B was sealed off from A at G. The reason for thus admitting air was to displace the vapour of the organic liquids from the connecting tube before sealing off: in this way perfectly clean seals were obtained, whereas the vapour, if present, carbonises when heated to redness. The vessel B was stored in a dark place until required.

*Filling of the Flotation Tubes.*—These tubes, of the form shown in Fig 2, were constructed of very thin-walled Durosil tubing of about 8 mm. bore, had a fine bent capillary at J, and were slightly constricted at L and K. The length of the tube between K and J was about 30 cm. Each tube bore an etched number corresponding with the sample of boric oxide it was to contain, and was charged with beads as follows: While dry air was passed through J up the perfectly clean and dry tube, beads, from 30—35 in number, of one sample of boric oxide were quickly removed from the phosphoric oxide desiccator and poured into this tube: the tube was then immediately sealed off first at L and then at J.

The procedure for filling the tubes with liquid was necessarily elaborate, but worked without a hitch in practice. A large aspirator bottle, containing a quantity of loose phosphoric oxide and air under slight pressure, was connected to the sealed tip of F (previously scratched with a file) by pressure tubing, through a train consisting of a tap, a phosphoric oxide guard-tube and a T-piece opening to the atmosphere by means of a tap and phosphoric oxide guard-tube on the side limb. The apparatus having been very thoroughly dried, pressure was raised in the aspirator and the whole was allowed to stand for over an hour to ensure adequate drying of the additional air. Thereafter the tip F was broken inside the rubber tube and the fine delivery tube I was also opened near the tip and at once inserted in a guard-tube carrying a current of dry air. Then each flotation tube in turn was cracked just below L by means of a sharp file and a hot rod, the top was lifted off, a fine bent tube delivering a current of dry air was passed down below the constriction K, and then the flotation tube was slipped quickly over

the jet I of the reservoir B, from which the guard-tube had been that instant removed. By admitting air from the aspirator, liquid was forced over from B until the flotation tube was filled to a depth of about 20 cm. The flow of liquid was stopped by shutting off B from the aspirator and releasing the pressure in B by opening to the air the guarded tap in the connecting train. Then the flotation tube was withdrawn from I (and replaced immediately by the guard-tube), the fine tube delivering air was lifted just above the constriction K, and the flotation tube was sealed with the blow-pipe at that point.

After the drill had been mastered by practice runs on blank apparatus, this procedure occupied much less time than it takes to describe. In the final experiments, the time required to fill a tube averaged four minutes, and no one tube was open for more than  $4\frac{1}{2}$  minutes.

*Determination of the Density and Thermal Expansion of the Liquid.*—For this purpose a special pycnometer of the form shown at M (Fig. 3) and holding about 10 c.c. was used. It had at N a taper ground carefully to fit both the cap, O, and the bent extension tube, P, and at R a fine engraved reference mark. Both tubes of the pycnometer were of very fine bore. It was weighed against a precisely similar pycnometer as tare, on a balance having a sensitivity of 20 scale divisions per mg., by means of a set of weights carefully calibrated in air for atomic weight work.

Five determinations of the weight of the pycnometer empty, made after various washings, fillings and immersions in the thermostat bath, gave concordant results, and thus afforded evidence that the error of weighing was probably insignificant. The weights of the pycnometer filled with pure water at  $17.00^{\circ}$  and  $19.45^{\circ}$  were determined in triplicate and thus, by means of the known specific volume of water, the absolute volume of the pycnometer at these temperatures was ascertained.

In filling the pycnometer with the flotation liquid the reservoir B (Fig. 3) was opened at Q, the carefully dried extension tube P (closed at the ground end by means of a rubber cap) was slipped in, and an air-tight joint made by sliding the wired-on rubber sleeve over the tube P. The reservoir was opened through a phosphoric oxide guard-tube at H. Both reservoir and pycnometer were then clamped to a retort stand and immersed over the barrels in the water of the thermostat tank maintained at  $17.00^{\circ} \pm 0.02^{\circ}$ . After 20 minutes, the retort stand was lifted from the bath, the pycnometer was connected by the ground joint N to the reservoir and filled with liquid forced over by admitting dry air through H. Then the pycnometer was disconnected and P was closed with its rubber cap.

These operations having been carried out very quickly, the stand and vessels were returned to the thermostat and held at  $17.00^{\circ}$  for a further 30 minutes. Then the liquid level in the pyknometer was adjusted by drawing off the excess with a piece of pure filter-paper, and the pyknometer was stoppered, removed from the bath, dried carefully, and weighed with all due precautions. It was then replaced in the thermostat, maintained at  $19.45^{\circ} \pm 0.02^{\circ}$  for 40 minutes, the liquid level was again adjusted, and the pyknometer was stoppered, dried, and weighed as before.

These determinations gave the data necessary to ascertain with the requisite precision the absolute density of the liquid at two temperatures, comprising between them the range of flotation temperatures. The density at intermediate temperatures was obtained on the assumption, clearly justifiable for so short a temperature range, that the relation of density to temperature is linear, and was read from a large-scale graph.

*Determination of Temperature of Flotation.*—The six flotation tubes, together with an open-scale thermometer graduated in  $0.1^{\circ}$ , were mounted vertically by means of rubber bands on two horizontal rods clamped to a retort stand. The whole apparatus was then immersed in a copper tank, with plate glass sides, containing about 27 litres of water. The tank was fitted with a motor-driven paddle, and at about room temperature this arrangement proved to be sufficiently thermostatic for its purpose. In a preliminary test, the temperature was raised slowly from about  $17^{\circ}$  to about  $19.5^{\circ}$  by the addition of quantities of 100 c.c. of hot water at regular intervals, and the approximate temperatures of flotation of the several samples of beads were observed. The final observations were made in each tube separately, and the temperature at which the beads remained suspended was noted for each sample. In all cases one or two beads—never more—whilst of the same order of density, appeared to be slightly heavier than the rest and sank first. The movement of the next lot in order of density, usually upwards of 6 (which were followed down almost immediately by the main bulk), was therefore observed with the aid of a fixed telescope, and the bath temperature was carefully regulated until they were brought to rest midway in their fall through the liquid. These beads were maintained stationary in suspension for 30 minutes and the temperature was observed every 3 minutes: these temperature readings did not vary over a greater range than  $0.02^{\circ}$  and the mean value was taken as the flotation temperature.

As the beads floated for  $\frac{1}{2}$  hour at a substantially constant temperature, it is evident that they must have been in thermal equilibrium with the liquid. Any small defect in this respect would have

a negligible effect on the results owing to the smallness of the thermal expansion of boric oxide glass. Samsoen (*Compt. rend.*, 1925, **181**, 354) has shown that up to  $240^{\circ}$  this has a value about  $15 \times 10^{-6}$ , whence a change of temperature of  $0.1^{\circ}$  (which is large in relation to the present measurements) changes the density of the glass by about one unit in the eighth decimal place.

Further, the prompt movement of the beads when the slightest perceptible change was made in the bath temperature showed that the flotation liquid within the tubes acquired the temperature of the bath with very little delay, probably within one minute. This is the more probable because other experiments in progress in these laboratories have shown that some 60—100 c.c. of liquid contained in a sealed tube 30 mm. in diameter with walls  $1\frac{1}{2}$  mm. thick, without agitation, requires only some 8—15 minutes to acquire within  $0.01^{\circ}$  the temperature of a water-bath in which it is wholly immersed.

### Results.

The following values for the density of the liquid, relative to water at  $4^{\circ}$ , are each the mean of two concordant determinations:—

Temperature .....	17.00°	19.45°
Volume of pycnometer .....	9.7822 c.c.	9.7825 c.c.
Weight of liquid contained by pycnometer ...	17.5858 g.	17.5471 g.
Density of liquid .....	1.79773	1.79372

The table given below shows for each sample of boric oxide the flotation temperature, the corresponding density, the atomic weight calculated from the density, and, in the case of three samples, the atomic weight derived from determinations of the ratio  $\text{BCl}_3 : 3\text{Ag}$  using boron trichloride prepared from the same original sample. In calculating the atomic weight corresponding to the ascertained density, sample 5, derived from boracite from Sultan Tchair, Asia Minor, was taken as standard, with the atomic weight  $B = 10.818$ . Hence for any other sample, X, the atomic weight is found by:

$$\text{At. wt. of boron in X} = \frac{1}{2} \left( \frac{\text{Density of X} \times \text{Mol. wt. of standard B}_2\text{O}_3 - 48}{\text{Density of standard B}_2\text{O}_3} \right).$$

Sample No.	Place of origin.	Flotation temp.	Density.	Relative atomic weight.	
				Calc. from density.	Determined from ratio $\text{BCl}_3 : 3\text{Ag}$ .
2	California	17.36°	1.79711	10.847	10.841
6	Tuscany	18.15	1.79583	10.823	10.825
5	Asia Minor	18.30	1.79558	10.818 (standard)	10.818
1	Chile	18.30	1.79558	10.818	
3	Argentina	18.65	1.79501	10.806	
4	Peru	19.25	1.79404	10.788*	

\* The beads of this sample showed a considerably greater variation in density among themselves than was observed in the case of the other samples. Hence the authors attach less weight to this figure than to the data for samples 1—5 inclusive.

*Discussion of Results.*

The method of determining densities here described may clearly be made to yield extremely precise results and is applicable to a great variety of solids, provided that a suitable flotation liquid can be obtained. The values recorded show that the mean density of pure fused boric oxide is 1.7952 and that the value 1.88 commonly used is considerably in error.

The estimated maximum error in the determination of the specific gravity of the flotation liquid is  $\pm 0.00008$ : the actual error is probably rather less at temperatures intermediate between 17.00° and 19.45°. Owing to the means adopted to ensure that all the flotation tubes were filled at one time from the same well-mixed bulk of liquid, the *relative* values of the specific gravity deduced from the flotation temperatures are probably uncertain only in so far as those temperatures are uncertain. It is unjustifiable to attempt to report in detail the very numerous and detailed records of the observations of flotation temperatures, but they have been subjected to the most critical examination by the three authors working independently and the utmost difference of opinion thus elicited in their interpretation would not affect by one unit the third decimal of the atomic weight in any case. Hence it seems probable that the relative densities have an error less than 1 part in 10,000 parts, and that the maximum error in the relative values of the atomic weight does not exceed four or five units in the third decimal.

Admitting the view here expressed as to the precision of these results, the observed differences among them require explanation. The authors believe that the samples of boric oxide are very pure and, moreover, that the uniformity so carefully observed in their purification and subsequent treatment should have ensured that any impurity, for example, a possible trace of water, which they may have retained can have had little influence on the *relative* values found for their densities. Hence the observed differences are attributed to a variation in the atomic weight of one of the elements present and as there exists no evidence that such variation is possible in the case of oxygen, it is assumed to occur in the atomic weight of boron. The good agreement in three cases between the relative atomic weights deduced from the density values and found by the determination of the ratio  $\text{BCl}_3 : 3\text{Ag}$  (Briscoe and Robinson, J., 1925, 127, 696) can scarcely be accidental, and the authors believe that the present work confirms the conclusions drawn in the paper cited.

If these atomic weight values are correct, it is remarkable that the atomic weights of boron from the Argentine and Peru are very appreciably lower than any values hitherto recorded.

Evidently a determination of the boron halide : silver ratio for material from these sources would constitute a valuable check on the present results and conclusions, and the authors have considered undertaking this investigation. It appears to them, however, that any further work they might do on the atomic weight of boron can add but little to the value of the evidence they have already advanced, and that they should now leave it to other chemists to confirm or refute the conclusion, drawn from that evidence, that boron, like lead, has an atomic weight varying with its source. It is much to be hoped that this further investigation will be undertaken.

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## XV.—*Butyl Esters of the Simpler Amino-acids.* *Part I.*

By WALTER THOMAS JAMES MORGAN.

HITHERTO, with few exceptions, only the ethyl esters of the amino-acids have been prepared and examined (Curtius, *Ber.*, 1883, 16, 753; 1884, 17, 953; *J. pr. Chem.*, 1888, 37, 150; Fischer, *Ber.*, 1901, 34, 433). Butyl esters have now been prepared. These are more stable than the corresponding ethyl esters—inasmuch as quantities up to 20 g. distil almost completely, whereas ethyl esters distilled under similar conditions invariably leave a brown residue—and are much less volatile in ether vapour under diminished pressure. They should be, therefore, the more suitable form in which the monoamino-acids produced by the hydrolysis of proteins may be estimated. Since the application of this method for the separation of the monoamino-acids of protein is now unavoidably postponed, it seems desirable to publish the work so far completed.

### EXPERIMENTAL.

*n*-Butyl Glycine Hydrochloride.—Glycine (5 g.) suspended in 100 g. of dried and carefully fractionated butyl alcohol was esterified by the method of Curtius (*Ber.*, *loc. cit.*). Several similar preparations of the hydrochloride were made using the dry lead salt of the acid. The finely divided lead chloride that separates has, according to Foreman (*Biochem. J.*, 1919, 13, 378), a favourable catalytic effect

on the rate of esterification. The mixture saturated with hydrogen chloride was heated on a boiling water-bath until the amino-acid dissolved, the excess of butyl alcohol was then distilled under reduced pressure, and the pale yellow syrup of the *ester hydrochloride* crystallised from ethyl acetate. The solid so obtained was quickly ground, kept for 2 days over solid potassium hydroxide, and crystallised from ether-ethyl acetate (1 : 2), separating in flat laminæ, m. p. 69—71°. (All melting-point determinations were carried out in sealed capillary tubes owing to the hygroscopic nature of the ester hydrochloride.) It dissolved readily in water, alcohol, acetone, or ethyl acetate, but was only sparingly soluble in ether or chloroform (Found : N, 8.2; Cl, 21.1.  $C_6H_{14}O_2NCl$  requires N, 8.3; Cl, 21.2%)\*.

*n-Butyl Glycine*,  $NH_2 \cdot CH_2 \cdot CO \cdot O \cdot C_4H_9$ .—To a vigorously shaken suspension of the hydrochloride (21.5 g.) in dry ether (250 c.c.) at 0°, anhydrous baryta was added, in portions of about 1 g., until it was in excess; even so, some hydrochloride remained, but this decomposed on addition of 5 c.c. of 70% potassium hydroxide solution. The whole was immediately shaken and filtered and the residue, consisting of baryta, barium chloride and a little undissolved ester, was shaken with two further quantities of ether. The combined ethereal filtrates were concentrated under reduced pressure to about 40 c.c., the temperature being kept below 30° to prevent volatilisation of the ester with the ether vapour. The ester distilled at 81—81.5°/18 mm. as a colourless oil having the characteristic odour of all amino-acid esters (yield, 14 g. or 83%;  $d_{16}^{20}$  0.9703). The ester is soluble in water, ether, or alcohol (Found : N, 10.6.  $C_6H_{13}O_2N$  requires N, 10.7%).

In a sealed glass tube, the freshly distilled ester (5 g.) changed completely in 24 hours into a white, crystalline solid. This substance gave an intense biuret reaction, charred without melting at 240°, and was insoluble in alcohol, chloroform, glacial acetic acid, or benzene but fairly easily soluble in hot water (Found in material washed free from butyl alcohol : C, 48.6; H, 7.7. Triglycylglycine butyl ester requires C, 47.7; H, 7.3%). A further preparation of this compound is being carried out, when it is hoped to recrystallise the substance and determine its molecular weight.

The *picrate* was prepared by warming together at 60° for  $\frac{1}{2}$  hour an alcoholic solution of the ester (3 g.) and a solution of picric acid (5.2 g.) in 50% alcohol. On cooling, the *picrate* separated in pale yellow laminæ, m. p. 113°, which were very soluble in acetone, somewhat soluble in chloroform or ether, and insoluble in light petroleum or ligroin (Found : N, 15.6.  $C_{12}H_{16}O_9N_4$  requires N, 15.5%).

The *benzoquinone* derivative,  $(C_4H_9 \cdot O \cdot CO \cdot CH_2 \cdot NH)_2C_6H_4O_2$ ,



separated in scarlet needles from the dark red solution produced by the interaction of the ester (3 g.) and benzoquinone (4 g.) in ether at 0°. The crystals were washed with ether and freed from quinol by dissolution in chloroform; the quinone compound, m. p. 179—180°, was precipitated from the solution by light petroleum (Found: N, 7.6.  $C_{18}H_{26}O_6N_2$  requires N, 7.6%).

*n*-Butyl carbamidoacetate,  $H_2N \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot O \cdot C_4H_9$ , separated in tufts of colourless needles, m. p. 119°, when butyl glycine hydrochloride (2.8 g.), dissolved in a minimum of water, was warmed with a solution of potassium cyanate (1.7 g.) on a water-bath. It was soluble in hot ethyl alcohol, sparingly soluble in cold acetone, and insoluble in light petroleum or ligroin (Found: N, 16.1.  $C_7H_{14}O_3N_2$  requires N, 16.2%).

*iso*Butyl Glycine Hydrochloride.—A suspension of glycine (15 g.) in dry *isobutyl* alcohol (250 c.c.) was saturated with hydrogen chloride, and solution completed by heating on a boiling water-bath for  $\frac{1}{2}$  hour. The subsequent procedure was as described in the case of the *n*-butyl ester hydrochloride. The *hydrochloride*, m. p. 84—88°, is very hygroscopic and quickly liquefies on exposure to air. It is readily soluble in alcohol or ethyl acetate, but only sparingly soluble in ether or chloroform (Found: N, 8.4; Cl, 21.2.  $C_6H_{14}O_2NCl$  requires N, 8.4; Cl, 21.2%).

*iso*Butyl glycine was obtained from its hydrochloride (37 g., recrystallised from ether-ethyl acetate [2:1] and dissolved in 750 c.c. of dry ether) in the same way as the normal ester. The ether was dried over anhydrous potassium sulphate. The pure *ester* is a colourless, oily liquid with a characteristic odour (yield, 73%), b. p. 79.5—80.5°/18 mm.,  $d^{20}_D$  0.9609,  $d^{17}_D$  0.9618. It is readily soluble in water, alcohol, or chloroform (Found: C, 54.9; H, 9.9.  $C_6H_{13}O_2N$  requires C, 55.1; H, 9.9%).

The *picrate* was obtained by warming together an alcoholic solution of the ester (2 g.) and an aqueous-alcoholic solution of picric acid (1 mol.) and pouring the mixture into water. The *picrate* was crystallised from benzene, dried in a vacuum desiccator, and, as the melting point was not sharp, recrystallised from alcohol and was thus obtained in needles, m. p. 82—87°. It was only slightly soluble in ether or light petroleum (b. p. 40—60°) and insoluble in ligroin (Found: N, 15.5.  $C_{12}H_{16}O_9N_4$  requires N, 15.5%).

The *benzoquinone* derivative was prepared and purified as was the preceding isomeride. The scarlet needles obtained, m. p. 171—172°, were insoluble in hot or cold water or ligroin, somewhat soluble in ether, and readily soluble in cold chloroform or 50% aqueous alcohol (Found: C, 59.2; H, 7.3; N, 7.7.  $C_{18}H_{26}O_6N_2$  requires C, 59.0; H, 7.1; N, 7.7%).

Unless stated otherwise, the following substances were prepared in essentially the same ways as the corresponding compounds already described.

*n*-Butyl dl-Alanine Hydrochloride.—Prepared from racemic alanine (15 g.) and recrystallised from ethyl acetate, this compound melted at 58–61° (sealed tube), rapidly deliquesced in moist air, and was only slightly soluble in ligroin or ether but readily soluble in ethyl alcohol, benzene, chloroform, or acetone (Found : N, 7.7; Cl, 19.5.  $C_7H_{16}O_2NCl$  requires N, 7.7; Cl, 19.6%).

*n*-Butyl dl-alanine was obtained as a colourless, oily liquid, b. p. 81.5–82°/16 mm.,  $d^{20}_D$  0.9342 (yield 66%), having the usual characteristic odour. It is soluble in water, ether, alcohol, or chloroform. After being kept in a sealed glass tube for 3 weeks, the ester showed no signs of anhydride formation (Found : N, 9.7.  $C_7H_{15}O_2N$  requires N, 9.6%).

The *picrate*, m. p. 124°, crystallised in needles from 30% and 50% alcohol and in opaque, dendritic crystals from 5% alcohol (Found : N, 14.7.  $C_{13}H_{18}O_9N_4$  requires N, 14.9%).

Several attempts were made to isolate the benzoquinone derivative. A solution of the ester and benzoquinone in dry ether developed a bright scarlet colour, but after cooling for several hours in a freezing mixture nothing separated; on cooling in solid carbon dioxide and ether, crystals of quinol were deposited. Evaporation of the ether solution gave only a red syrup which could not be crystallised. Precipitation with light petroleum gave only a dark red oil. The isolation of this compound is being further studied.

*iso*Butyl dl-Alanine Hydrochloride.—The syrup obtained was very difficult to crystallise even after drying in a vacuum desiccator over phosphoric oxide. Precipitation with ether of a solution of the hydrochloride in ethyl acetate gave a syrupy liquid which crystallised in flat, soft, soapy plates, m. p. 60–63° (sealed tube), which changed into a syrup on being exposed to air for a few minutes (Found : N, 7.6.  $C_7H_{16}O_2NCl$  requires N, 7.7%).

*iso*Butyl dl-alanine, prepared from the ester hydrochloride (31 g.) and distilled at 77–78°/19 mm., was a colourless, oily liquid soluble in water, alcohol, ligroin, or chloroform (yield 95%);  $d^{20}_D$  0.9330 (Found : N, 9.7.  $C_7H_{15}O_2N$  requires N, 9.6%).

As in the case of the *n*-butyl ester, all attempts to isolate the quinone derivative failed.

The *picrate* was obtained quantitatively in small, flat plates, m. p. 132–133°, by warming the ester (2.5 g.) with a solution of picric acid (3.6 g.) in 50 c.c. of 50% alcohol at 70–80° for  $\frac{1}{2}$  hour and cooling over-night. It was soluble in alcohol, ether, or acetone,

sparingly soluble in chloroform, and insoluble in light petroleum or ligroin (Found : N, 15.1.  $C_{13}H_{18}O_9N_4$  requires N, 15.0%).

*n-Butyl dl-Valine Hydrochloride*.—Prepared from *dl*-valine (5 g.) and crystallised from ethyl acetate, the *hydrochloride* was obtained in colourless, deliquescent needles, m.p. 59—60°, which were readily soluble in alcohol or acetone and sparingly soluble in dry ether or light petroleum (Found : N, 6.7.  $C_9H_{20}O_2NCl$  requires N, 6.7%).

*n-Butyl dl-valine* was obtained from the hydrochloride (3.5 g.) in the usual way; the combined ethereal filtrates were dried with anhydrous sodium sulphate and the ether was evaporated below 25°. The *ester*, b. p. 98—98.5°/17 mm.,  $d^{20}_4$  0.9266, was a colourless, syrupy liquid (yield 97.5%) having the usual characteristic odour. It was soluble in water, alcohol, ether, or chloroform (Found : N, 8.3.  $C_9H_{19}O_2N$  requires N, 8.1%).

The *picrate* formed long, yellow needles, m. p. 91—92°, which were soluble in acetone, ether, or chloroform, somewhat soluble in benzene, and insoluble in light petroleum (Found : N, 13.9.  $C_{15}H_{22}O_9N_4$  requires N, 13.9%).

*n-Butyl dl-Leucine Hydrochloride*.—Leucine (6 g.) was esterified in the usual manner. After standing in the ice-chest for 48 hours, the alcoholic solution deposited flat, colourless plates, which were recrystallised from ether and dried in a vacuum desiccator; m. p. 110—111°. The *hydrochloride* was exceedingly hygroscopic, and very soluble in alcohol but only slightly soluble in chloroform or ether. It crystallised from ethyl acetate in stellate clusters of colourless needles (Found : N, 6.4; Cl, 16.0.  $C_{10}H_{22}O_2NCl$  requires N, 6.3; Cl, 15.9%).

*n-Butyl dl-leucine*, prepared from the hydrochloride (4 g.), was a clear, colourless, oily liquid (yield 69%), b. p. 113.5°/18 mm.,  $d^{18.5}_4$  0.8733, which was soluble in water, alcohol, ether, or chloroform (Found : N, 7.4.  $C_{10}H_{21}O_2N$  requires N, 7.5%).

The *picrate* was obtained in yellow needles, m. p. 139°, which were soluble in alcohol, ether, or acetone and insoluble in ligroin or benzene (Found : C, 46.1; H, 13.6.  $C_{16}H_{24}O_9N_4$  requires C, 46.2; H, 5.8; N, 13.5%).

*isoButyl dl-Leucine Hydrochloride*.—This compound was a clear, colourless syrup which slowly crystallised on standing for 2 or 3 days over solid caustic potash in a vacuum desiccator; it was recrystallised from ethyl acetate, washed with ether, and again dried in a vacuum desiccator (yield 81%); m. p. 97—99° (Found : N, 6.3; Cl, 15.7.  $C_{10}H_{22}O_2NCl$  requires N, 6.3; Cl, 15.9%).

*isoButyl dl-leucine*, b. p. 110°/19 mm.,  $d^{18.5}_4$  0.9066, was obtained as a colourless, oily liquid (yield 88%) which was soluble in alcohol,

chloroform, or ether (Found : C, 64.1; H, 11.0; N, 7.4.  $C_{10}H_{21}O_2N$  requires C, 64.2; H, 11.2; N, 7.5%).

The *picrate* crystallised from dilute alcohol in flat plates, m. p. 135—136°, which were soluble in hot water, chloroform, or ethyl alcohol, slightly soluble in cold water or ether, and insoluble in light petroleum (Found : C, 46.0; H, 6.0; N, 13.6.  $C_{16}H_{24}O_9N_4$  requires C, 46.2; H, 5.8; N, 13.5%).

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## XVI.—*The Nitration of $\beta$ -Naphthoic Acid and Some New Amino- and Nitro-naphthoic Acids.*

By HAROLD AINSWORTH HARRISON and FRANK ALBERT ROYLE.

### *The Nitration of $\beta$ -Naphthoic Acid.*

THE earliest work on the nitration of  $\beta$ -naphthoic acid was carried out by Kuchenmeister (*Ber.*, 1870, **3**, 740), and by Ekstrand (*ibid.*, 1879, **12**, 1393), but yielded little if anything of permanent value. Later, Ekstrand (*J. pr. Chem.*, 1890, **42**, 273), by fractional crystallisation of the mixture of ethyl esters obtained from the crude nitration product, isolated five supposedly distinct compounds. Of these, one (m. p. 111°) gave a free acid, m. p. 295°, which was identical with that previously prepared by Graeff (*Ber.*, 1883, **16**, 2252) from the nitration product of  $\beta$ -naphthonitrile, and was shown to be 8-nitro-2-naphthoic acid. The second ester (m. p. 121°; free acid, m. p. 288°) was that of 5-nitro-2-naphthoic acid. From the small fractions which remained, one ester melting at 75° was isolated (free acid, m. p. about 285°), and two others were described in the following year (*ibid.*, 1891, **43**, 409); of these, one melted at 92° (free acid, m. p. 272° [279°] \*) and the other at

\* This nitro-acid on reduction gave an aminonaphthoic acid, m. p. 211°. Now 5-amino-1-naphthoic acid melts at this temperature, and the 5-nitro-isomeride is to be expected from the nitration of  $\alpha$ -naphthoic acid, if any occurred as impurity in Ekstrand's initial material. Further, 8-nitro-1-naphthoic acid, which would also be formed, cannot be esterified by the method employed (hydrogen chloride in alcoholic solution; compare Ekstrand, *ibid.*, 1888, **38**, 156) and therefore would not appear in the esterified mixture. Finally, the ethyl ester of 5-amino-1-naphthoic acid melts at 92° (compare above). The free nitro-acid, however, melts at 242° (Graeff, *loc. cit.*, p. 2250).

131°. (This last ester charred when warmed with sulphuric acid in the usual way, and the corresponding nitro-acid was not isolated.) No constitutions were assigned by Ekstrand to these isomerides.

Of the seven possible mononitro-derivatives of  $\beta$ -naphthoic acid, Ekstrand had thus claimed to have detected the presence of five. These did not include the 1-nitro-compound, m. p. 239°, which has since been prepared by Mayer and Oppenheimer (*Ber.*, 1918, 51, 1239). The characteristics of this derivative as described by these authors do not coincide with those of any of Ekstrand's supposed nitronaphthoic acids.

Repetition of Ekstrand's experiments, using his second method of nitration (*i.e.*, in absence of any solvent), has shown that approximately equal amounts of 5- and 8-nitro-2-naphthoic acids are formed in at least 95% combined yield. Some low-melting indeterminate fractions of the esters resulting from the use of alcohol or benzene as crystallising medium were all easily resolved by employing ethyl acetate and light petroleum. With regard to Ekstrand's highest-melting ester (m. p. 131°) which charred with sulphuric acid, it is to be noted that the ethyl ester of 7-nitro-2-naphthoic acid (prepared by the present authors at a later stage) melts at 131°, but can be hydrolysed quite easily to give a quantitative yield of the nitro-acid. No trace of this ester was detected in the nitration product.

In addition to the 5- and 8-nitro-isomerides, we have succeeded in establishing the presence of traces of 1-nitro-2-naphthoic acid in the nitration mixture.\* This acid cannot be esterified by the passage of hydrogen chloride into an alcoholic solution, and consequently was easily separated from the reaction material. It was never obtained quite pure, but reduction with ferrous sulphate and ammonia produced an aminonaphthoic acid, m. p. 202–205° (decomp.), the *acetyl* derivative of which crystallised from alcohol in long, gorse-like needles, m. p. 184°. This was identical with an authentic specimen of 1-acetylamino-2-naphthoic acid prepared synthetically (see Friedländer and Littner, *Ber.*, 1915, 48, 330).

During the nitration of  $\beta$ -naphthoic acid, therefore, between 60–80° with excess of nitric acid (*d* 1.42) only 5-nitro-2-naphthoic acid (m. p. 291° instead of 288°) and 8-nitro-2-naphthoic acid

\* Ekstrand (*ibid.*, 1890, 42, 273) digested the mixture of nitro-acids with sodium hydroxide during an attempt to separate them by fractionation of their sodium salts. But Friedländer and Littner (*Ber.*, 1915, 48, 330) have proved that hydrolysis of 1-nitro-2-naphthonitrile by alkaline reagents (even barium hydroxide) causes the replacement of the nitro-group by a hydroxyl group, and this also takes place in the case of the acid. It is therefore probable that Ekstrand had destroyed any 1-nitro-compound present.

(m. p. 295°) are formed in large quantity, together with a trace of 1-nitro-2-naphthoic acid.

*Some New Amino- and Nitro-naphthoic Acids.*

Of the seven theoretically possible amino-derivatives of  $\alpha$ -naphthoic acid, only four (the 2-, 4-, 5-, and 8-amino-1-naphthoic acids) have hitherto been prepared. Even fewer of the nitro- $\alpha$ -naphthoic acids are known, since no compound containing one nitro-group in any of the four  $\beta$ -positions is recorded. Of the substituted derivatives of  $\beta$ -naphthoic acid, only one amino-acid, the 6-derivative, had not been prepared, but there were still four unknown nitro-isomerides, *viz.*, the 3-, 4-, 6- and 7-nitro-2-naphthoic acids.\* As a result of the present work, 6- and 7-amino-1-naphthoic acids, 6-amino-, 6- and 7-nitro-2-naphthoic acids have been obtained for the first time.

The method adopted for the preparation of these aminonaphthoic acids consists in heating the neutral sodium salt of the corresponding hydroxynaphthoic acid † with ammonia and bisulphite under pressure. Möhlau and Kriebel (*Ber.*, 1895, 28, 3096) had already employed strong ammonia (without bisulphite) to convert 3-hydroxy-2-naphthoic acid into the amino-acid. Repetition of their experiment, however, showed no appreciable conversion, either with the 3-isomeride or any other. Neither could the 3-amino-compound be obtained when bisulphite was used, though the conditions were varied over a wide range.  $\beta$ -Naphthylamine was the sole product of reaction, as it was also from the anilide of 3-hydroxy-2-naphthoic acid (naphthol A.S.). Similarly, 1-hydroxy-2-naphthoic acid yielded  $\alpha$ -naphthylamine.

In addition to the new aminonaphthoic acids mentioned, 5- and 8-amino-2-naphthoic acids have also been prepared by the use of the bisulphite modification.

All the amino-2-naphthoic acids thus obtained were converted into nitronaphthoic acids by treatment of the diazotised product with copper powder and excess of sodium nitrite, as described by Veselý and Dvořák (*Bull. Soc. chim.*, 1922, 31, 421; 1923, 33, 319). The 5- and 8-nitro-2-naphthoic acids so prepared were used

\* Mention is made (*A.*, 1923, 124, i, 119) of a nitronaphthoic acid, m. p. 225—227°, obtained by Ruzicka and Stoll (*Helv. Chim. Acta*, 1922, 5, 923) as a by-product in the oxidation of 2-methyl-8-isopropyl-naphthalene with dilute nitric acid, the main product being 2 : 8-naphthalenedicarboxylic acid. The nitronaphthoic acid in question is really a nitro-8-isopropyl-2-naphthoic acid; the abstract is somewhat misleading.

† For the details of preparation of the various hydroxynaphthoic acids see Butler, Royle, and Schedler (*J.*, 1923, 123, 1641, 1649).

to confirm the identity of the nitration products of  $\beta$ -naphthoic acid (see previous section).

#### EXPERIMENTAL.

*Conversion of Hydroxy-acids into Amino-acids.*—The hydroxy-naphthoic acid (15 g.) is dissolved in water with the aid of sodium bicarbonate (6.3 g.); ammonia (100 c.c.,  $d$  0.88) is added, followed by a solution, saturated at 15°, of sulphur dioxide in water (25 c.c.). The whole is diluted with water (110 c.c.), and heated in an autoclave at 200–210° (pressure about 50 atmospheres) for 10 hours. The solution is boiled to drive off most of the ammonia, filtered, and slightly acidified by the gradual addition of acetic acid. Under these conditions 5- and 8-amino-2-naphthoic acids separate in a very satisfactory condition. With 6-amino-2-naphthoic acid (and to a less extent with 6- and 7-amino-1-naphthoic acids) it is advisable to add an excess of warm dilute hydrochloric acid to the acetic acid solution. After extraction with ether to remove impurities, the solution is concentrated and the amino-hydrochloride allowed to crystallise. The free acid is regenerated by dissolving in a small quantity of sodium carbonate solution and carefully neutralising with acetic acid. 7-Amino-2-naphthoic acid is best isolated through its difficultly soluble sodium salt, by the addition of sodium hydroxide to the autoclave liquor after removal of excess of ammonia. The yield in every case is almost theoretical.

The various aminonaphthoic acids differ but slightly from one another as regards their solubilities. They are easily soluble in alcohol or acetic acid, somewhat less easily soluble in ether, acetone or ethyl acetate, and very sparingly soluble in benzene.

*6-Amino-1-naphthoic acid* crystallises from alcohol in light brown aggregates, m. p. 203° (Found: C, 70.4; H, 4.8.  $C_{11}H_9O_2N$  requires C, 70.6; H, 4.8%). The *hydrochloride* crystallises from water in clumps of needles, and the *acetyl* derivative from alcohol in white needles, m. p. 170–172°.

*7-Amino-1-naphthoic acid* crystallises from alcohol in light brown prisms, m. p. 223–224° (Found: C, 70.3; H, 5.0%). The *hydrochloride* separates from water in warty clusters of needles, and the *acetyl* derivative from alcohol in almost white needles, m. p. 229–230°.

*6-Amino-2-naphthoic acid* crystallises from dilute alcohol in very pale yellow needles, m. p. 225° \* (Found: C, 70.8; H, 4.7%).

\* Since this work was completed a compound described as "6-amino-2-naphthoic acid" has been obtained by Dzięwoński, Schoenówna, and Waldmann (*Ber.*, 1925, 58, 1211). These authors give the melting point as 222–223°; but the acetyl derivative, from which the free amino-acid

The *hydrochloride* is not very soluble in cold but rather more soluble in hot water, crystallising in small flakes. The *acetyl* derivative separates from dilute alcohol or from acetone in white needles, m. p. 230—232°.

7-Amino-2-naphthoic acid crystallises from alcohol in pale yellow leaflets, m. p. 245°. Its *acetyl* derivative separates from dilute alcohol in almost white, flat needles, m. p. 200—201° (decomp.).\*

*Types of Fluorescence shown.*

Solvent.	$\alpha$ : 6-.	$\alpha$ : 7-.	$\beta$ : 4-.	$\beta$ : 5-.	$\beta$ : 6-.	$\beta$ : 7-.	$\beta$ : 8-.
Alcohol	Green	Emerald green	Blue	Green	Purple	Sea green	Emerald green
Ether	Light blue	Emerald green	Royal blue (Blue)	Cobalt blue (Green)	Purple	Pale blue	Turquoise blue
Acetic acid	Pale violet	Bluish-green			Cobalt blue	Bluish-purple (Blue)	Leaf green
Benzene	Royal blue	Sky blue	Bluish-purple	Light blue	Violet blue		Greenish-blue
Ethyl acetate	Turquoise blue	Turquoise blue	Blue	Greenish-blue	Reddish-violet	Blue	Bluish-green
Acetone	Greenish-blue	Turquoise blue	Royal blue	Turquoise blue	Reddish-violet	Blue	Bluish-green

A few of these fluorescences require magnesium light or the light from an iron arc to render them visible; such are indicated by brackets. The majority are very marked, even in subdued daylight. The colours given in the table are those induced by arc light; they vary slightly in one or two instances from the fluorescences in daylight.

In addition to the preceding observations on the fluorescent properties of aminonaphthoic acids taken under approximately standard conditions, 1-amino-2-naphthoic acid furnishes an appreciable blue fluorescence in alcohol, ether, or acetic acid, while 3-amino-2-naphthoic acid (according to Möhlau and Kriebel, *loc. cit.*) gives a green fluorescence in alcohol or ether.

It is worthy of note that the aminonaphthoic acids whose configurations correspond to those of possible naphthaquinones produce more intensely fluorescent solutions than those not having a potentially quinonoid structure; e.g.,  $\beta$ : 8- is stronger than  $\beta$ : 5-;  $\beta$ : 6- than  $\beta$ : 7-; and  $\alpha$ : 7- than  $\alpha$ : 6-.

was prepared, melts at 271—272°. It is to be observed that the configuration of this isomeride was only arrived at by a process of exclusion. On the other hand, the constants given do not coincide with those of any other amino-2-naphthoic acid, all of which are now known.

\* It is important to carry out the melting-point determinations of these acetyl derivatives in a standardised manner, in order to ensure concordant results. No method other than the one here described gives a definite fluid melt. The tube is inserted when the temperature of the bath is only about 5° below the expected m. p. of the substance, and the time taken for the necessary rise in temperature must be less than 2 minutes. Incipient softening usually precedes liquefaction, and on increasing the temperature the substance reverts to the solid state, melting a second time, though not sharply, at a somewhat higher temperature. (To suggest that the m. p.—271—272°—recorded in the previous note is really this higher melting point would be somewhat premature, since the range is limited to 1°.)



*Conversion of Amino-acids into Nitro-acids.*—The aminonaphthoic acid (8 g.) is dissolved in warm glacial acetic acid (30 g.), and sulphuric acid (16 g.), diluted with an equal volume of water, added with constant stirring. The sulphate which separates is at once diazotised at 0° with sodium nitrite (3.5 g.) dissolved in water (15 c.c.). The clear diazo-solution is poured in small portions into a solution of sodium nitrite (35 g. in 140 c.c. of water) containing also clean copper bronze (30 g.). The reaction liquor, on standing at room temperature for 4 hours with regular shaking, deposits the whole of the nitronaphthoic acid, which is filtered off and purified by repeated extractions with boiling alcohol (charcoal). The filtered alcoholic solution is concentrated to a small bulk; the addition of water then precipitates the nitronaphthoic acid as a yellow powder. The total yield is about 0.5 g.

6-Nitro-2-naphthoic acid crystallises from alcohol in pale yellow plates, m. p. 310° (Found: C, 60.5; H, 3.4.  $C_{11}H_7O_4N$  requires C, 60.8; H, 3.2%). The ethyl ester, m. p. 177°, crystallises in brownish-yellow, rectangular plates from ethyl acetate, in needles from alcohol. The acid can be recovered from the ester by hydrolysis with strong sulphuric acid on the water-bath for a few hours.

7-Nitro-2-naphthoic acid crystallises from alcohol in yellow needles, m. p. 262° (Found: C, 60.6; H, 3.4%). It is moderately soluble in acetic acid, but dissolves with difficulty in other solvents. The ethyl ester crystallises from alcohol in pale salmon-coloured, silky needles, m. p. 131°. This ester shows no sign of charring when hydrolysed with sulphuric acid in the usual way (compare Ekstrand's ester, m. p. 131°; see p. 85).

One of us (H. A. H.) desires to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant, and to the Research Fund Committee of the Chemical Society for a grant for chemicals. We are also indebted to Professor Lapworth for his interest in the work.

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## XVII.—A Revision of the Structural Formula of Glucose.

By WILLIAM CHARLTON, WALTER NORMAN HAWORTH, and  
STANLEY PEAT.

THE discovery of the methylglucosides and the interpretation of the phenomena of mutarotation of sugars furnished the strongest reasons for the allocation of an oxide ring structure to the mono-

saccharides, and this formulation has been universally accepted. Tollens first ascribed to glucose a heterocyclic structure, and this conception was adopted by Fischer, who represented the normal methylglucosides by a five-membered or pentaphane ring, constituting the  $\gamma$ -oxide formula, which is the current and generally recognised basis for the formulation of sugars.

The methylglucosides were isolated in  $\alpha$ - and  $\beta$ -stereochemical forms, and it was shown that corresponding to these there existed also  $\alpha$ - and  $\beta$ -modifications of glucose. In 1914, Fischer (*Ber.*, 47, 1980) prepared a new methylglucoside which differed profoundly in stability from the  $\alpha$ - and  $\beta$ -modifications. This he described as " $\gamma$ "-methylglucoside. The nomenclature he adopted seemed unfortunate inasmuch as in this case the Greek letter was not intended to have any stereochemical significance but merely represented a third or novel form. Fischer recognised that the new variety of methylglucoside was a structural isomeride, and thus the term  $\gamma$ -sugar introduced in this connexion had no essential relationship to the  $\gamma$ -lactones. Confusion has naturally arisen from the use of this terminology, and especially so since the term " $\gamma$ -oxide form" was already applied to the normal sugars.

An experimental basis for the definite allocation to glucose of a  $\gamma$ -oxide (butylene oxide) constitution rather than that of any other oxide or heterocyclic structure was definitely lacking. Assuming, however, the spatial distribution of the oxygen valencies to be similar to those of carbon, and applying the considerations arising from the Baeyer strain theory, it was apprehended that a five-membered ring would involve the least strain in the sugar molecule, and this type of ring should, therefore, be capable of easy formation. It is tacitly assumed here that the conditions of strain in such a ring would be analogous to those in *cyclopentane*, where the carbon atoms carry only hydrogen. These conditions seemed to be supported by the facility with which sugars give rise to lactones, and by the properties which the latter display suggesting their resemblance to  $\gamma$ -lactones. Kiliani and Kleemann (*Ber.*, 1884, 17, 1300) attempted to obtain direct proof of the structure of gluconolactone, but it was left to Hudson to furnish, by his brilliant theoretical studies, the most convincing evidence of the  $\gamma$ -lactonic nature of the products of the oxidation of sugars.

In considering twenty-four lactones of the sugar series derived from the corresponding polyhydroxy-monobasic acids, Hudson (*J. Amer. Chem. Soc.*, 1910, 32, 345) found that if it were postulated that ring formation occurred at the  $\gamma$ -carbon atom, a remarkable parallelism was exhibited between the position of the lactone ring

and the sign of the rotation of the lactone, and that there were no cases of disagreement on the basis of this hypothesis. On the other hand, it was demonstrated that if this linking occurred at the  $\alpha$ -,  $\beta$ -, or  $\delta$ -carbon atom, the number of cases of disagreement with this "rule" were found to be 8, 10, and 12, respectively, out of the twenty-four lactones examined. He calculated that, on the theory of probability, the chances are 17 millions to one that the lactone will have the lactonic ring engaging the  $\gamma$ -carbon atom. This conclusion is supported by an abundance of other cases, and in the absence of direct synthetic evidence to the contrary, this view of the constitution of lactones derived from unsubstituted sugars must be adopted.

It has, however, been too readily assumed that an analogy should be drawn between this principle of lactone ring formation and the type of ring structure existing in the parent sugars. In instituting the inquiry of which details are given in this communication, the present authors have attempted to test the validity of the latter assumption.

It was considered that there should be recognisable differences in stability between lactones of the usual  $\gamma$ -type and those having a smaller or larger number of atoms than five constituting the ring, and that these differences would be reflected in a variation both in the rate and in the extent of hydrolysis to the open-chain acid. During the past 4 years the necessary synthetic materials and the data for this comparison have been accumulated, and in recent communications some of these results have been recorded by one of us without reference, however, to their essential bearing on the present problem.

The degree of accuracy attainable by direct titration of aqueous solutions of the lactones was insufficient for the purpose indicated. A more sensitive method of comparison was provided by studying the polarimetric changes accompanying ring scission from lactone to open-chain acid, using either aqueous or alcohol-water solutions.

Polarimetric data furnished by the completely methylated lactones derived from glucose, galactose, mannose, arabinose, and xylose led to a recognition of two types. Those lactones prepared from the normal forms of these sugars, by first methylating the aldoses and then submitting them to oxidation with bromine water, exhibited a rapid diminution or increase in specific rotation when dissolved in water or aqueous alcohol. Conversely, those lactones prepared from the labile or  $\gamma$ -sugars displayed a very slow and much less marked change in specific rotation.

*Observed Changes in the Specific Rotation of the Lactones  
from the following Sugars (aqueous solutions).*

	$\gamma$ -Forms (Time, 20 days).	Normal forms (Time, 24 hrs.).	Nos. of Curves.
Tetramethyl glucose ...	+61.5° $\rightarrow$ 39.6°	+101.1° $\rightarrow$ 25.6°	i and ii
Tetramethyl galactose ...	-27.1° $\rightarrow$ 25.2°	+161.5° $\rightarrow$ 27.2°	iii and iv
Trimethyl arabinose ...	-42.2° $\rightarrow$ 25.1°	+145° $\rightarrow$ 22.4° *	v and vi
Trimethyl xylose .....	+74.1° $\rightarrow$ 61.4°	-3.8° $\rightarrow$ +20.8° (Time, 7 days)	vii and viii
Tetramethyl mannose.	+65.2° $\rightarrow$ 56.3°†	+105° $\rightarrow$ 45.6°	

\* This value was determined by Pryde, Hirst, and Humphreys (*J.*, 1925, 127, 348).

† This figure is explained in the text, since it was obtained by Levene and Meyer from methylated mannonolactone. The time intervals are not recorded.

The curves given in Fig. 1 are those of the lactones related to glucose, galactose, and arabinose. Inspection of these curves suggests that the lactones represented by i, iii, and v are of the same type, and that those shown by ii, iv, and vi belong to a second and distinct type.

This second series illustrates the polarimetric data given by the lactones prepared from the normal forms of tetramethyl glucose, tetramethyl galactose and trimethyl arabinose, which exhibit a marked decline in specific rotation when dissolved in water. The equilibrium between the cyclic compound and open-chain acid is speedily reached and hydrolysis is also more nearly complete as revealed by direct titration at this stage.

On the other hand, the first series (Nos. i, iii, and v) represents lactones prepared from the labile or  $\gamma$ -sugars, and it is seen that the initial rotations are lower and that a much less profound change in the optical values occurs. Moreover, equilibrium between lactone and hydroxy-acid is only attained after several weeks, and at this stage hydrolysis is not nearly so complete as in the case of the former series.

The curves shown in Fig. 2 differ in a similar sense, but not in the same degree; the steeper of the two represents the lactone from normal trimethyl xylose, whilst the remaining curve, which is almost linear, is given by the lactone from trimethyl  $\gamma$ -xylose.

Fortunately, it is possible to correlate these data with constitutional formulæ which have been already determined for several of these sugars and their derived lactones, but for reasons which will be outlined later the constitution of the two glucoses and their gluconolactones had not yet admitted of any proof.

The method which is adopted in this communication shows that the data now recorded render it possible to reach a reasonable

conclusion as to the structure of glucose and its  $\gamma$ -derivatives by observing the analogy which is found to subsist between their lactones and those of the other sugars of known constitution.

Of the four sugars examined (five, including mannose), two have been subjected to close constitutional study by direct methods

FIG. 1.

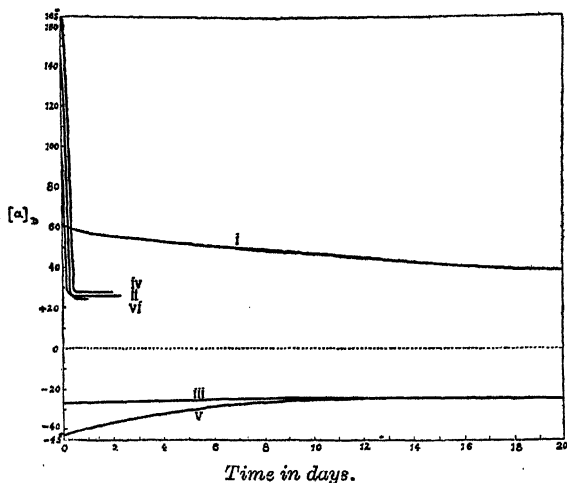
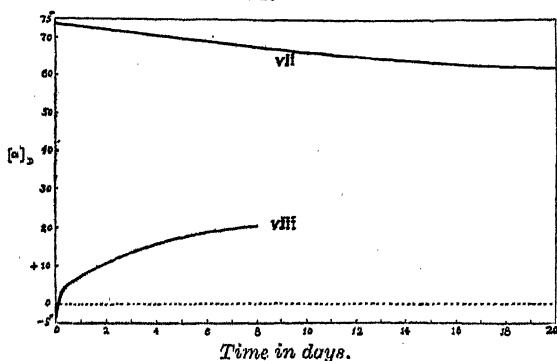
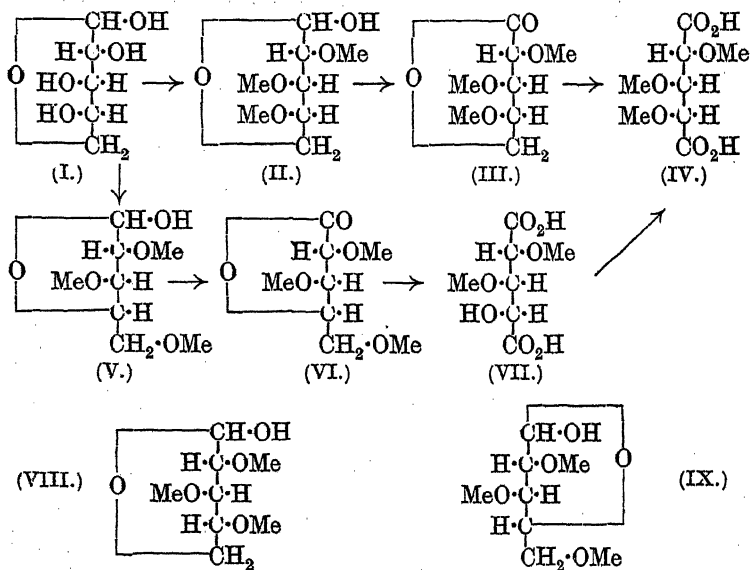


FIG. 2.



of oxidation. Thus Hirst and Robertson (J., 1925, 127, 358) have demonstrated that the normal form of trimethyl *L*-arabinose must have the constitution (II), since it gives the dibasic acid (IV), namely, arabo-trimethoxyglutaric acid; and, since the properties of the trimethyl arabinose are in every respect similar to those of natural arabinose, the latter is given the constitution (I).

Another form of trimethyl arabinose was prepared by Baker and Haworth (J., 1925, **127**, 365), and this may be described as the " $\gamma$ "-sugar. The formula (V) was allocated to this compound, since it gave rise to the levorotatory lactone (VI) and, on further oxidation, to the dibasic acid (VII) which contained only two methoxyl residues. This latter, on complete methylation, was identical with Hirst and Robertson's acid (IV).

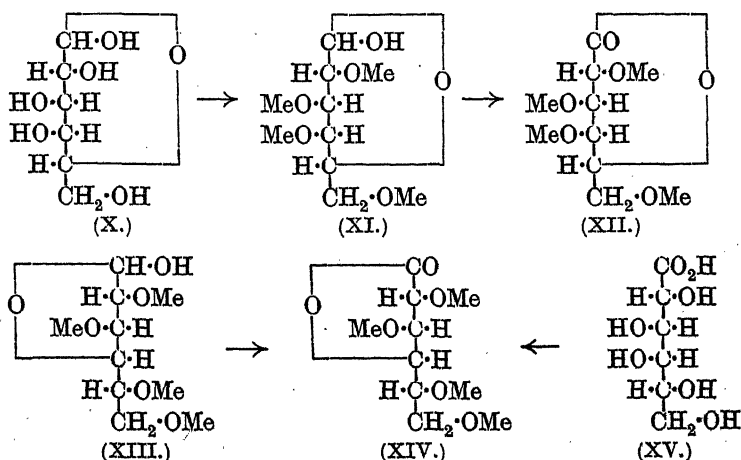


The same constitutional relationships have been established also for normal trimethyl xylose (VIII) (Hirst and Purves, J., 1923, **123**, 1352), which is found to give on oxidation the xylo-trimethoxyglutaric acid, stereoisomeric with the acid of formula (IV); and in a forthcoming paper by Haworth and Westgarth the preparation will be described of trimethyl  $\gamma$ -xylose, to which is allocated the structural formula (IX) analogous to that ascribed above (V) to trimethyl  $\gamma$ -arabinose.

Taking the two examples of the pentoses, xylose and arabinose, it is clear that the normal sugars are amyleno-oxidic in structure, and that the labile or  $\gamma$ -forms are butyleno oxides. The related lactones are therefore  $\delta$ -lactones for the normal sugars and  $\gamma$ -lactones for the labile or  $\gamma$ -sugars.

Coming now to the case of galactose, it must be stated that the evidence as to structure depends here on Hudson's rule. Pryde (J., 1923, **123**, 1808) has shown that normal tetramethyl galactose (XI) changes to tetramethyl- $\delta$ -galactonolactone (XII) on oxidation,

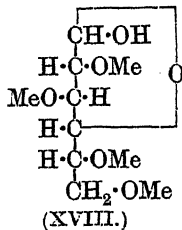
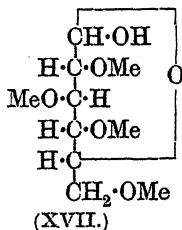
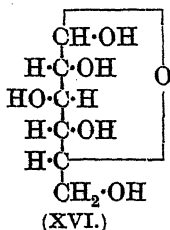
and therefore normal or naturally occurring galactose is given the constitution (X). The corresponding labile or  $\gamma$ -sugar (XIII) was prepared by Haworth, Ruell, and Westgarth (J., 1924, 125, 2468) and this on oxidation gave rise to the  $\gamma$ -lactone (XIV), which is also obtained on passing from ordinary or normal galactose or from galactonic acid (XV) to its lactone. The rotations of the compounds resulting from all these transformations are completely in accord with Hudson's rule, which, it may be emphasised, requires that galactonolactone must be a  $\gamma$ -lactone (see p. 90).



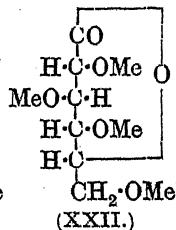
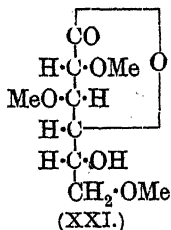
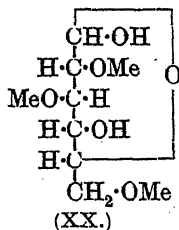
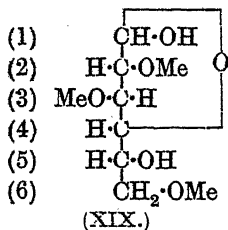
Similarly, mannose has been shown to conform to the above structural scheme. Levene and Meyer (*J. Biol. Chem.*, 1924, 60, 167) found that normal tetramethyl mannose gave a lactone,  $[\alpha]_D + 105^\circ \rightarrow 45.6^\circ$ , whilst methylation of the lactone from mannonic acid led to the isolation of a different and crystalline tetramethyl mannolactone having  $[\alpha]_D + 65.2^\circ \rightarrow 56.3^\circ$ . These optical values will be found to be closely similar to those quoted later for  $\delta$ - and  $\gamma$ -lactones, respectively, but as the authors did not record the intermediate rotation values at short period intervals the curves could not be included in Figs. 1 and 2.

It only remains, therefore, to apply this analogy to the lactone from normal tetramethyl glucose, which is indicated by the remaining curve (ii) in this series. This conforms definitely to the same type as the other three (Nos. iv, vi, and viii), and we therefore regard it as a  $\delta$ -lactone, and the normal tetramethyl glucose is therefore considered to be amylene-oxidic and consequently we assign to it the structural formula (XVII), whence glucose has the formula (XVI).

The other curves in Figs. 1 and 2, Nos. i, iii, v, and vii, clearly belong to a different category from those already discussed. All these represent the lactones prepared from the methylated " $\gamma$ "-sugars. We have demonstrated that, since three of the four substances are  $\gamma$ -lactones, the sugars from which they are prepared are butylene-oxidic in structure, and by analogy the curve No. i is considered to be that of tetramethyl  $\gamma$ -gluconolactone, whence it follows that tetramethyl  $\gamma$ -glucose should be given the constitution (XVIII).



A second line of argument as to the constitution of glucose is provided by evidence drawn from the study of 2:3:6-trimethyl glucose. This sugar has been repeatedly examined and the relative positions of its three methyl groups are definitely determined (Denham and Woodhouse, J., 1914, 105, 2361; Haworth and Leitch, J., 1918, 113, 191; Haworth and Hirst, J., 1921, 119, 193; Irvine and Hirst, J., 1922, 121, 1213). We are concerned only with the ring structure of this compound, which, if the argument already presented in this paper be accepted, should now be revised from that indicated by formula (XIX) to the new formula (XX).



Now it is known (Haworth and Hirst, *loc. cit.*) that the sugar is converted on further methylation into normal tetramethyl glucose and earlier in this paper the structural formula (XVII) has been ascribed to the latter on the ground that the derived lactone is a  $\delta$ -lactone (XXII).

Inspection of the two alternative formulæ (XIX and XX) sug-



gests, however, a possible application of this sugar as a means of testing the validity of this reasoning and of the conclusions already drawn. Thus this sugar on oxidation to the monobasic acid offers a choice of two free hydroxyl positions for the attachment of the lactone ring, namely, those on carbon atoms (4) and (5) (formula XXI), and this applies no matter which of the two sugar formulæ is the correct one.

Adopting Hudson's rule, this choice must be restricted to that of the  $\gamma$ -lactone (XXI). If now this trimethyl  $\gamma$ -gluconolactone should, on complete methylation, be shown to be identical with that tetramethyl gluconolactone derived from normal tetramethyl glucose, then the latter sugar (and therefore glucose also) would be butylene-oxidic in structure and the formula hitherto generally accepted for glucose would continue to hold.

In the actual event this was found not to be the case; it was observed that 2:3:6-trimethyl glucose gave a gluconolactone (XXI) which on methylation was identical with the tetramethyl  $\gamma$ -gluconolactone derived from the labile or  $\gamma$ -form of tetramethyl glucose (XVIII), and therefore the constitutional formula for the latter is substantiated, and fresh support is provided for the argument outlined in the former part of this communication.

Moreover, the crystalline phenylhydrazides of the tetramethyl gluconolactones from the three sources were prepared and analysed, and the following are the data for the melting points:

*Phenylhydrazides of tetramethyl gluconolactones.*

	M. p.	Mixed m. p. with (c).
(a) From normal tetramethyl glucose .....	109—112°	102—118°
(b) From tetramethyl $\gamma$ -glucose .....	131—134	130—133
(c) From 2:3:6-trimethyl glucose .....	130—133	

Thus we again reach the conclusion that ordinary glucose should be given the formula (XVI). This assumes that ordinary free glucose is identical in structure with normal tetramethyl glucose, but this is shown to be the case because  $\alpha$ - and  $\beta$ -methylglucosides give crystalline tetramethyl glucose on methylation followed by hydrolysis, as do those natural di-, tri-, and poly-saccharides which contain the glucose residue, and moreover, E. F. Armstrong has shown that  $\alpha$ - and  $\beta$ -glucose are stereochemically parallel to  $\alpha$ - and  $\beta$ -methylglucosides.

All the commonly occurring aldoses are therefore shown to exist normally as amylene- or 1:5-oxide forms, or, reverting to the older nomenclature which we prefer, they may now be described as  $\delta$ -oxides. So far this has been shown to apply to glucose,

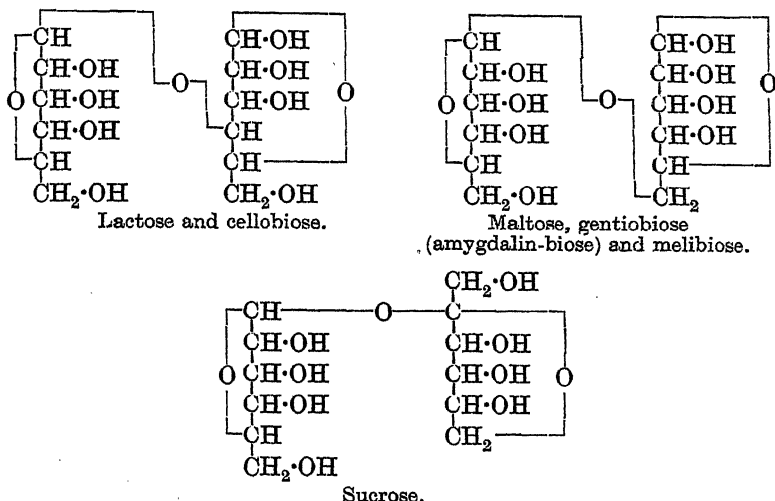
galactose, mannose, arabinose, and xylose. By a curious coincidence the so-called " $\gamma$ "-sugars of the aldose type, which have now been shown to give rise to  $\gamma$ -lactones, may be more accurately described as  $\gamma$ -oxides, since they exist as butylene- or 1 : 4-oxide forms.

There remain to be mentioned the ketoses, and the constitutional study here has been confined to fructose, which occurs naturally as a  $\gamma$ -form in sucrose, raffinose, and inulin. The results of oxidation experiments conducted on tetramethyl  $\gamma$ -fructose derived from sucrose indicate that, in this sugar, an amylen- or  $\delta$ -oxide ring is present (Haworth and Linnell, Haworth and Mitchell, J., 1923, 123, 294, 301). On the other hand, Irvine and Patterson (J., 1922, 121, 2696) have examined the constitution of the normal form of tetramethyl fructose, which is crystalline, and which has not yet been isolated from a naturally occurring carbohydrate. This sugar they found to have the structure of a butylene- or  $\gamma$ -oxide. Thus, in the series of the ketoses, the position as compared with the aldoses would seem to be reversed, in that the labile sugar is the  $\delta$ -oxide form, and the normal sugar the  $\gamma$ -oxide. It would therefore appear that, in nature, both aldoses and ketoses occur as amylen- or  $\delta$ -oxides, a result which is in keeping with the simplest view of the synthesis of sucrose in the plant.

If this revision of the structural formula of glucose be accepted and applied to other carbohydrates, many fundamental readjustments are rendered necessary. Thus the constitutional formulæ allocated to natural di- and tri-saccharides by one of the present authors are directly implicated, as are also those suggested for starch and cellulose by other workers. These compounds will now require to be formulated as possessing  $\delta$ -oxide rings in each hexose residue. In the case of lactose and cellobiose this change also involves a displacement of the point of attachment of the hexose chains from a position associated with the fifth carbon atom to that of the fourth.\*

Leaving out of account the stereochemical relationships, it is now possible to represent the principal disaccharides by three formulæ :

\* It is, however, possible to regard one glucose residue in each of these disaccharides as existing as a  $\gamma$ -oxide or  $\gamma$ -sugar, in which case the earlier constitution will continue to hold with respect to the position of the biase linking, but this is an unlikely contingency. That 2 : 3 : 6-trimethyl glucose can pass into a  $\gamma$ -oxide form is extremely probable, and indeed we have some evidence of this. It is important to notice, however, that the sugar 2 : 3 : 5-trimethyl glucose must now be regarded as 2 : 3 : 4-trimethyl glucose, and that normal crystalline tetramethyl glucose is now 2 : 3 : 4 : 6-tetramethyl glucose.



## EXPERIMENTAL.

*Tetramethyl δ-Gluconolactone*.—This lactone was prepared by oxidising normal crystalline tetramethyl glucose with bromine water under the usual conditions (Purdie and Irvine, J., 1903, 83, 1021). It was then dissolved in a slight deficiency of *N*/10-sodium hydroxide, and the aqueous solution evaporated at 35–40° under diminished pressure. The residue of sodium tetramethyl gluconate was triturated thrice with dry chloroform to remove traces of unoxidised sugar and other impurities and the remaining solid was filtered, washed with chloroform, dried, and weighed. An aqueous solution of the salt was then decomposed by adding the equivalent of dilute hydrochloric acid from a burette. Isolation of the purified lactone was effected by evaporation under diminished pressure, followed by extraction from the semi-solid residue with dry ether. The tetramethyl δ-gluconolactone distilled completely at about 100°/0.05 mm. and showed  $n_D$  1.4532. *Titration*. 0.1355 g. required 6.05 c.c. of 0.0965*N*-NaOH (Calc., 6.02 c.c.).

A titration was also conducted after keeping an aqueous solution of the lactone for 24 hours; it then appeared that more than 90% had been converted into the open-chain acid.

Determinations of the rotation of the lactone were recorded as follows:

In ethyl alcohol ( $c = 3.65$ ),  $[\alpha]_D + 101.1^\circ$ .

In aqueous alcohol (38% EtOH) ( $c = 1.39$ ):

Time in hours .	0.25	2	5	21	25	66	
$[\alpha]_D$ .....	+90.3°	84.0°	68.0°	40.7°	38.4°	38.4°	constant

In water ( $c = 1.37$ ) :

Time in hours .	0.1	3	5	6.5	8.25	26.25
$[\alpha]_D$ .....	+88.5°	43.2°	31.4°	25.6°	25.6°	25.6° constant

*Phenylhydrazide Derivative.*—This was obtained by heating for 3 hours at 100° phenylhydrazine (1 mol.) with the above lactone (1 mol.). The crystals which appeared on cooling were recrystallised from ether and light petroleum and melted at 109–112°. On admixture with the phenylhydrazide of the  $\gamma$ -lactone as prepared below under (A) and (B), (m. p. 130–133°) the melting point for the mixture was depressed to 102–118° (Found : C, 56.1; H, 7.6; N, 8.0.  $C_{16}H_{26}O_6N_2$  requires C, 56.1; H, 7.6; N, 8.2%).

*Tetramethyl  $\gamma$ -Gluconolactone.*—(A) In one experiment, 4.3 g. of 2:3:6-trimethyl glucose were oxidised with bromine water and the corresponding lactone was isolated in the usual way. This product was purified by extraction with light petroleum, which dissolved the lactone, leaving as residue traces of unchanged sugar. *Titration.* 0.0943 g. required 4.24 c.c. of  $N/10$ -NaOH (Calc., 4.48 c.c.) (Found : OMe, 40.9. Calc., OMe, 42.2%).

The tetramethyl gluconolactone was obtained by twice methylating the above product with Purdie's reagents and was thereafter distilled. It showed  $n_D$  1.4470 (Found : C, 51.6; H, 7.8; OMe, 53.5. Calc., C, 51.3; H, 7.7; OMe, 53.0%). *Titration.* 0.0945 g. required 3.86 c.c. of  $N/10$ -NaOH (Calc., 4.03 c.c.).

In a second experiment, using a highly purified specimen of 2:3:6-trimethyl glucose, the tetramethyl  $\gamma$ -gluconolactone distilled at 92–96°/0.02 mm. and the colourless liquid was dissolved in a slight excess of aqueous barium hydroxide, left over-night, and then heated at 70° for 1 hour. Thereafter the excess of barium hydroxide was precipitated by admitting carbon dioxide, the filtrate evaporated under diminished pressure, and the residue extracted with ether to remove impurities. Solution of the barium salt in water containing the requisite equivalent of hydrochloric acid led to the isolation of the purified  $\gamma$ -lactone, which showed  $[\alpha]_D = +49.7^\circ$  in ethyl alcohol ( $c = 2$ ), and on dilution with water (44%) this value changed in 3 hours to  $+48.9^\circ$ , and thereafter showed little change during 2 days. A titration showed that at this stage about 30% of the lactone had been converted into the acid.

*The phenylhydrazide* was prepared by adopting the same procedure as that described below. The product was washed with petroleum, and recrystallised from ether. M. p. 130–133° (Found : C, 56.05; H, 7.8; N, 8.2. Calc. for  $C_{16}H_{26}O_6N_2$ , C, 56.1; H, 7.6; N, 8.2%).

(B) The above lactone was also prepared from tetramethyl  $\gamma$ -glucose (Irvine, Fyfe, and Hogg, J., 1915, 107, 529), the precaution being taken to separate any traces of the normal sugar

by the method of hydrolysing the methylglucoside with *N*/15-hydrochloric acid, since acid of this concentration has little effect on the normal glucosides but effects the complete hydrolysis of the  $\gamma$ -form. The  $\gamma$ -sugar was oxidised with bromine water in the usual way, and the above lactone distilled as a colourless liquid, b. p.  $97^{\circ}/0.05$  mm.,  $n_D$  1.4467. In ethyl alcohol ( $c = 2.07$ ) the specific rotation was  $+53.7^{\circ}$ , and on dilution with water (44%) the reading was  $[\alpha]_D = +49.8^{\circ}$ , falling to  $48.9^{\circ}$  in 4 hours, at which value it remained constant for 2 days.

The polarimetric data were recorded for an aqueous solution of the lactone.

Time in hours ...	0.16	1.33	5.06	19.33	43.83
$[\alpha]_D$ .....	$+61.5^{\circ}$	$60.7^{\circ}$	$57.2^{\circ}$	$56.2^{\circ}$	$55.6^{\circ}$
Time in days .....	6	7	12	15	20
$[\alpha]_D$ .....	$+48^{\circ}$	$47.4^{\circ}$	$44.0^{\circ}$	$39.6^{\circ}$	$39.6^{\circ}$

*Phenylhydrazide*.—The lactone was heated during 3 hours at  $100^{\circ}$  with an equivalent proportion of phenylhydrazine. The product had crystallised during this period, and the crystals were purified from light petroleum and dry ether. M. p.  $131-134^{\circ}$ . In admixture with the specimen of the phenylhydrazide prepared as described above (A) there was no depression of the melting point (Found: C, 56.2; H, 7.8; N, 8.2%).

*Tetramethyl  $\delta$ -Galactonolactone*.—The specimen prepared by Haworth, Ruell, and Westgarth (*loc. cit.*) was purified and used in the following determinations of specific rotations in water ( $c = 0.95$ ):

Time in mins. ...	19	40	70	100	165	220	280	340
$[\alpha]_D$ .....	$+161.1^{\circ}$	$146.3^{\circ}$	$122.1^{\circ}$	$98.9^{\circ}$	$62.1^{\circ}$	$46.3^{\circ}$	$36.8^{\circ}$	$32.6^{\circ}$
Time in hours ...	7	8	10	22	46			
$[\alpha]_D$ .....	$28.4^{\circ}$	$28.2^{\circ}$	$27.4^{\circ}$	$27.2^{\circ}$	$27.2^{\circ}$			

*Trimethyl  $\gamma$ -Arabonolactone*.—The crystalline specimen used was that prepared by Baker and Haworth (*loc. cit.*). The solvent was water.

Time in days .....	0	4	10	20
$[\alpha]_D$ .....	$-42.0^{\circ}$	$33.8^{\circ}$	$26.0^{\circ}$	$25.1^{\circ}$

Other optical data employed in constructing the curves given in the introduction will be found by consulting the references quoted.

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XVIII.—*Studies in Adsorption by an Optical Method.*  
*Fixation by Dispersoids of Methylene-blue within*  
*the Disperse Phase.*

By ANDOR FODOR and RASSA RIWLIN.

ADSORBENTS in a comparatively coarse state of division, and therefore readily separable from the solution, have hitherto been used in investigations on adsorption. When one comes to deal with colloidal, finely divided adsorbents—and there is no doubt that the micelle of a sol also can act as an adsorbent—the difficulty of separating the phases from one another becomes almost insurmountable. Scarcely any case of this kind has been thoroughly examined because of the experimental difficulties. Dynamic methods, which cause a displacement of the equilibrium, and ultrafiltration are useless. The applicable static methods are limited in number. Potentiometric and conductivity methods, useful as they are in the case of proteins, which adsorb relatively large quantities of electrolytes, can be employed to measure the adsorption of only a few definite ions, and the method of compensation-dialysis has many disadvantages, one of which is the disturbance due to the membrane. For these and other reasons, it seemed to the authors that an optical method would be the most suitable for measuring adsorption, and, since the polarimeter and the refractometer cannot deal with opaque or turbid liquids, it should be based upon the absorption of light.

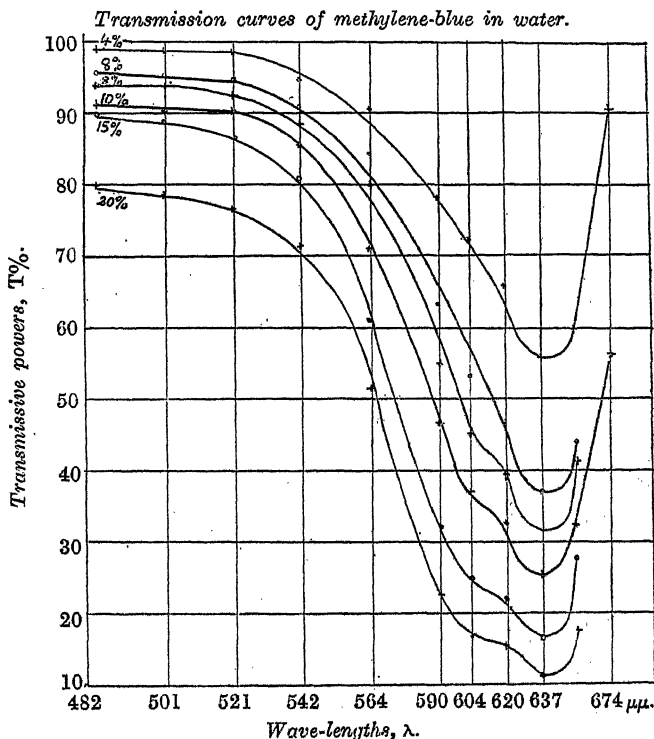
The concentration of a dye in solution will diminish on addition of a colloidal solution, owing to adsorption of the dye by the micelle. The absorption curves of the dye solution before and after the addition will therefore not be the same; and the difference between them will be a measure of the adsorption, if other losses of light, *e.g.*, by diffusion, do not affect the result.

A suitable dye solution must comply with the following requirements: 1. It must be stable. 2. Its absorption spectrum must (a) fall within the visual region and not be too extended, and (b) be continuous and consist of one band. The curve will then have only one maximum or minimum, in the neighbourhood of which slight changes can be very conveniently measured.

*Method.*—The transmissive powers,  $T$ , of a dye solution for light of different wave-lengths were measured directly in percentages with Vierorath's improved form of the Schmidt-Haensch spectrophotometer. The transmission curve of the solution was then obtained by plotting the values of  $T$  as ordinates and wave-lengths ( $\lambda$ ) as abscissæ (Fig. 1).

The concentration of a dye solution may be determined by this method in the following way, which obviates the application of Beer's law. The absorption curves of a series of solutions of the dye of known concentrations are drawn. The minima of these curves will all lie on one and the same ordinate, *viz.*, that drawn through the wave-length corresponding to minimum transmissive power. A second graph is drawn, having the concentrations of the

FIG. 1.



solutions as abscissæ and the corresponding minimal transmissive powers as ordinates. The minimal transmissive power of the solution of unknown concentration is now determined from its transmission curve, and the corresponding abscissa in the second graph will then give the concentration.

#### EXPERIMENTAL.

*Preparation of the Dye Solutions.*—A series of solutions was prepared containing 4, 6, 8, 10, 12½, 15, 17½, 20, 25, 30, 40, and 50% \*

\* For convenience' sake, a true concentration of 0.000n% is written as n%.

of a standard solution of methylene-blue (0.1 g. in 1000 c.c. of water). Ten c.c. of each of those solutions were mixed with 10 c.c. of water, and the transmission curves of the mixtures were plotted (Fig. 1). From time to time, the transmissive powers were redetermined to ensure that they still agreed with those of the freshly prepared solutions, and therefore that the concentrations of methylene-blue were unchanged.

Methylene-blue is adsorbed by many substances, including filter-paper. The solutions, therefore, were not filtered and the parts of the vessels used that would come into contact with the liquid were specially polished.

Solutions of methylene-blue are not very stable. Under the influence of light and air they slowly lose their colour, and much more quickly in presence of alkali. The mixture of methylene-blue and a sol under investigation was therefore compared with a solution having the same hydrogen-ion concentration. Wherever possible, for the preparation of the comparison liquid the same acid or alkali was used as that present in the sol.

In many cases the sol itself was cloudy. The effect of the consequent scattering of light was ascertained in the following way. The transmissive power ( $a$ ) of a mixture of 10 c.c. of the sol with 10 c.c. of water was measured. If  $c$  is the transmissive power of the methylene-blue solution (10 c.c. of the diluted standard solution + 10 c.c. of water) and  $b$  that of the experimental mixture (10 c.c. of the diluted standard solution of methylene-blue + 10 c.c. of the sol), then, provided that there was no interference due to chemical reaction or adsorption, for each wave-length,  $ac = b$ .

If the sol transmitted light to the same extent as water,  $a = 1$ ; and to find any deviation from the 'mixture' law, it was only necessary to compare  $c$  with  $b$ .

TABLE I.

Transmissive powers of methylene-blue + silica sol.

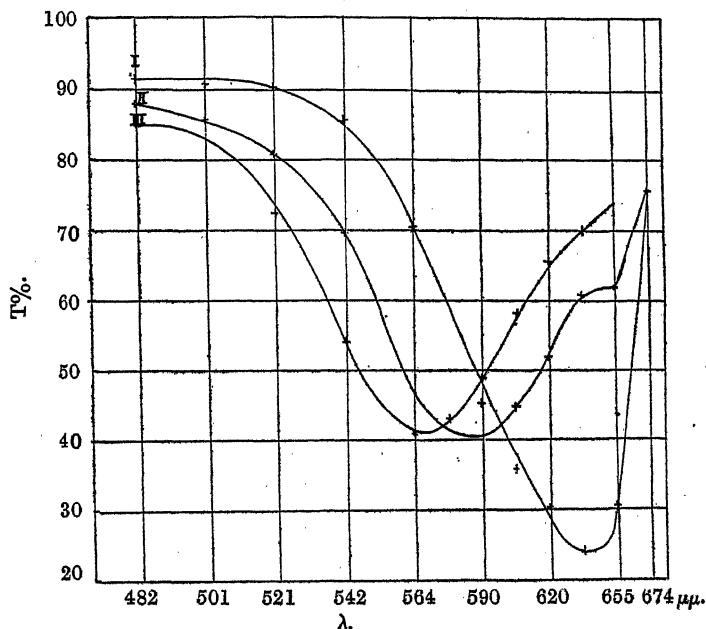
$\lambda$ ( $\mu$ ).	% Conc. of methylene-blue.						
	4.	6.	8.	10.	12.5.	15.	17.5.
482	95	93	89.5	87.5	85	83	80
501	95.5	92.5	89	85.5	83	80	75
521	94	89.5	84.5	81	79	75	69.5
542	84	79.5	74.5	69	64	58	52
564	70	60	53	45	40	35	30
590	65.5	55	47.5	40	34.5	25	22
604	74.5	61	53.5	44.5	40	30	26.5
620	80.5	69.5	60	51.5	45.5	40	35
637	85	77	68	60	55	46	42
655	86	79	70	61	57.5	49	44
674	90	85	82	75	—	65	—



1. *Silica Sol*.—This was prepared by Ostwald's method ("Kleines Praktikum der Kolloidchemie," 3rd ed., p. 8, expt. 23).  $a = 1$  for all wave-lengths.

The transmissive power of the reddish-violet mixture of the methylene-blue solution with the silica sol (Fig. 2, curve II) is quite different from that of its blue mixture with water (curve I); the minimum has shifted from  $\lambda 637 \mu\mu$  to  $\lambda 590 \mu\mu$  and is of about twice the magnitude. Moreover, the two transmission curves have

FIG. 2.



I, *Methylene-blue + water*. II, *Methylene-blue + silica sol*.  
 III, *Methylene-blue + silica sol + sodium hydroxide*.

different forms. These facts all indicate the production of a compound.

To prove that the effect of the sol on the methylene-blue was not due to the presence of hydrogen- or hydroxyl-ions, the transmission curves were determined of methylene-blue solutions containing these ions. It will be seen (Table II) that the addition neither of acid nor of alkali caused any considerable alteration in the position of the minimum of the curve for the methylene-blue solution during the time of observation. If the solutions were kept for some time, the minimum shifted towards the blue end of the spectrum (see last two columns). Acid was without appreciable effect

TABLE II.

Effect of acid or alkali on the transmissive powers of methylene-blue.

$\lambda$ ( $\mu$ ).	12.5% Methylene-blue.			17.5% Methylene-blue + N/10-NaOH.		
	+ Water.	+ N/10-HCl.	+ N/10-NaOH.	Soon after mixing.	After 2 hrs.	After 24 hrs.
482	91.5	91	90.5	79	79	61.5
501	92	91.5	89.5	75	75	55
521	91.5	90	89.5	69	67.5	45
542	85	85	83	55	55	35
564	70	68.5	70	40	39.5	29.5
590	46	39.5	51	29	29	25
604	36	30	41	25.5	25	48.5
620	31.5	25	35.5	24.5	25.5	65
637	25.5	20	29.5	23.5	29	75
655	32	26	35	28.5	37.5	80

on the transmissive power of the mixture of methylene-blue solution and silica sol, whilst the addition of alkali caused the point of inflexion in the region of  $\lambda = 637 \mu$  (Fig. 2, curve II) almost to disappear and the minimum to shift to  $\lambda = 564 \mu$  (curve III).

When a mixture of methylene-blue solution and silica sol was kept in an unpolished vessel, there was little if any adsorption of the dye on the walls. It seems as if the dye is so strongly held by the particles of sol that it is indifferent to any other influence.

An experiment with kaolin gave somewhat similar results: Mixtures of 10% methylene-blue solution with (a) water, (b) silica sol, and (c) 1% sodium silicate solution were each shaken with 100 mg. of kaolin, which was then allowed to settle. The supernatant liquid was (a) colourless, (b) violet-blue, (c) blue.

In another experiment, 2, 3, 5, 10, 30, and 50% solutions of methylene-blue were each mixed with 10 c.c. of silica sol and shaken with 100 mg. of kaolin. After settling, the sediment was coloured in every case, the liquors from the 2% and 3% solutions were colourless, and the others were slightly coloured.

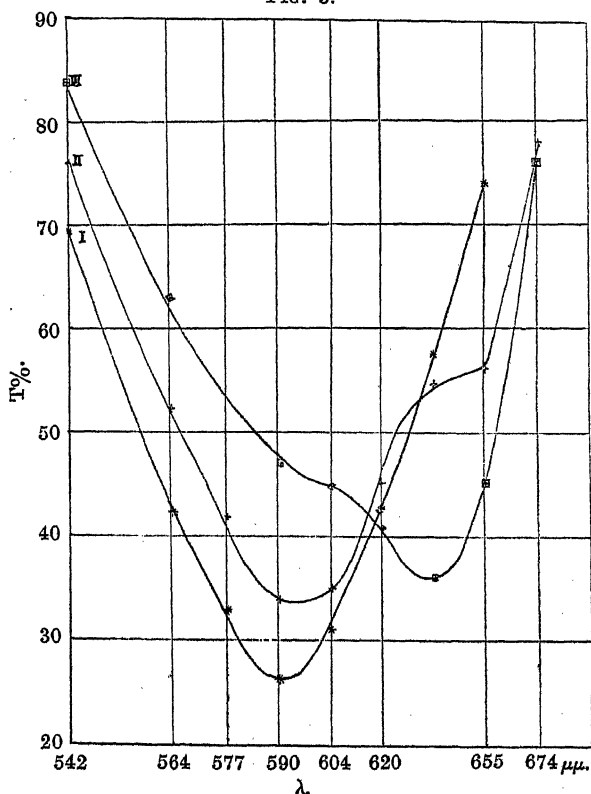
*Sodium Silicate* (Merck's commercial solution).—When the last experiment was repeated with a 1% solution of sodium silicate instead of the silica sol, even the liquors from the 2% and 3% solutions of methylene-blue were coloured. Sodium silicate seems to retain the dye better than silica sol.

On mixing solutions of methylene-blue and sodium silicate a blue precipitate was obtained or not according as the former or the latter was in excess. A similar behaviour was not observed in the case of the silica sol.

The transmission curves of mixtures of solutions of methylene-blue and sodium silicate were determined; the solutions were of

course alkaline. As in the case of the silica sol (Fig. 2, curve II), a minimum was found at  $\lambda$  590  $\mu\mu$  (Fig. 3, curve I). On addition of insufficient hydrochloric acid for neutralisation the minimum was slightly displaced and a bend appeared in the region of  $\lambda$  637  $\mu\mu$  (curve II). When the mixture was made acid, the minimum shifted to  $\lambda$  637  $\mu\mu$ , its place being taken by a slight bend (curve III). If the

FIG. 3.



I, *Methylene-blue + sodium silicate + water.* II, *Methylene-blue + sodium silicate + hydrochloric acid (still faintly alkaline).* III, *Methylene-blue + sodium silicate + hydrochloric acid (faintly acid).*

acid was added very carefully until the mixture was neutral, the whole mass coagulated.

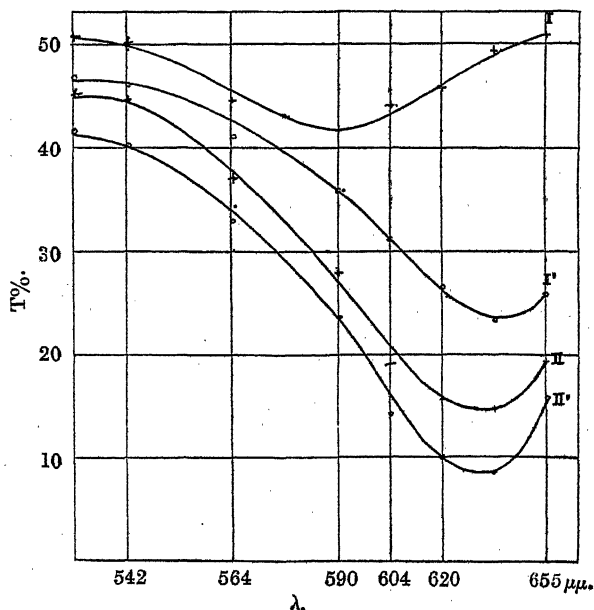
*Kaolin.*—A suspension of 2 g. of kaolin in 100 c.c. of water was kept for 18 hours, and the turbid liquor was then syphoned off. This liquor, containing only the finest particles of the kaolin, was used in the following experiments and was well shaken before each determination.

TABLE III.

Transmissive powers of mixtures of methylene-blue and kaolin.

$\lambda$ ( $\mu$ ).	Me-b (6%) + kaolin.			Me-b (10%) + kaolin.			Me-b (15%) + kaolin.		
	a.	ac.	b.	a.	ac.	b.	a.	ac.	b.
482	48	46	50	50	46	49	47	42	45.5
501	47.5	45.5	50.5	49.5	45.5	49	47	42	46
521	48.5	46	50.5	49	44	49	48.5	41.5	45
542	51	46	50	51	44.5	48	50	40	44.5
564	51.5	42	45	52	38	42.5	53.5	33	37.5
590	57	36	41.5	58	26	37	54.5	18	22
604	58	30.5	44	59	21	36	55	14	19.5
620	60	27	45.5	61	18	35	57	11.5	17
637	63	23.5	49	62	15.5	35	60	9	15
655	63	27	50.5	64	19	39	60	16.5	20

FIG. 4.



I=b for the mixture 6% methylene-blue+kaolin. I'=ac for the mixture 6% methylene-blue+kaolin. II=b for the mixture 15% methylene-blue+kaolin. II'=ac for the mixture 15% methylene-blue+kaolin.

The transmissive powers of the kaolin suspension (a), of the methylene-blue solution (c), and of the mixture of the two (b) were determined and b was compared with ac (Table III and Fig. 4). The b transmission curves and the calculated ac curves are almost parallel for the more concentrated solutions of methylene-blue, but diverge in the case of dilute solutions. The b curve, however, invariably lies above the corresponding ac curve, and therefore it

TABLE IV.

Transmissive power of methylene-blue (10%).

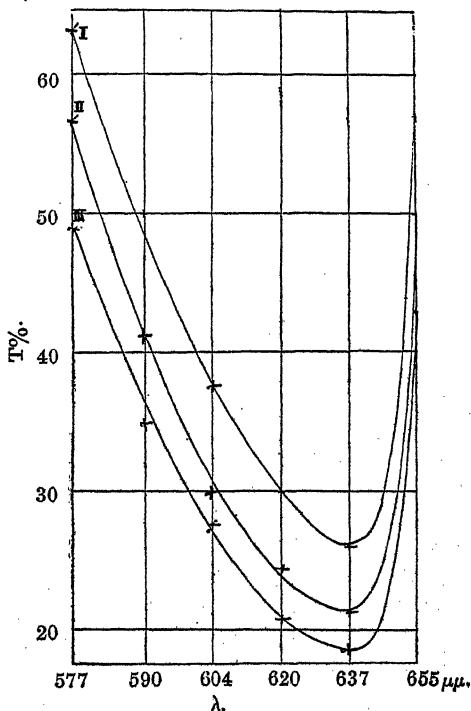
$\lambda$ ( $\mu$ ).	+ Water	+ N/50-Acetic acid.	+ Aluminium hydroxide sol.
577	63	57	49
590	50	41	35
604	37.5	30	28
620	30	24.5	21
637	26	21	18.5
655	57	50	42.5

may be concluded that the methylene-blue is partly adsorbed by the kaolin.

#### Aluminium Hydroxide

*Sol.*—The sol was prepared by Ostwald's method (*op. cit.*, p. 12, expt. 30). A mixture of methylene-blue solution and the sol was less transparent than the corresponding mixture of methylene-blue and water. This result was due to the presence in the sol of acetate ions, which diminish the transmissive power of methylene-blue (Table IV and Fig. 5). Almost identical transmission curves were obtained for the methylene-blue solution + the aluminium hydroxide sol and methylene-blue solution + an acetate buffer the  $p_H$  of which was the same as that of the sol (3.84).\* No adsorption of methylene-blue, therefore, can be demonstrated in the case of aluminium hydroxide sol.

FIG. 5.



I, 10% methylene-blue + water. II, 10% methylene-blue + N/50-acetic acid. III, 10% methylene-blue + aluminium hydroxide sol.

*Natural Protein.*—A solution of white of egg in water (20 vols.)

\* Compare A. Fodor, "Determination of the affinity constants of weak acids and bases" ("Handbuch der biologischen Arbeitsmethoden," E. Abderhalden, p. 474).

was filtered. The filtrate was turbid, and therefore *a* had to be determined. On comparing *ac* (where *c* = transmissive power of methylene-blue + buffer solution) with *b*, no difference was observed (Table V). Natural protein, therefore, does not adsorb methylene-blue.

TABLE V.

Transmissive power of white of egg + methylene-blue (10%).

$\lambda$ ( $\mu$ ).	<i>a</i> .	<i>c</i> .	<i>ac</i> .	<i>b</i> .	$\lambda$ ( $\mu$ ).	<i>a</i> .	<i>c</i> .	<i>ac</i> .	<i>b</i> .
482	92	93	85.5	86	590	95	47.5	45	44
501	93.5	93	87	86	604	95	35	33	34
521	93.5	92.5	86.5	85.5	620	95	29	27.5	28.5
542	94	84.5	79.5	78	637	95.5	24	23	24
564	95	70.5	67	69.5	655	96	33.5	32	34.5

An experiment was also made with the protein at the isoelectric point. Acid was added in increasing quantities to solutions of the protein, and the concentration was thus found (*viz.*, 0.6 c.c. of *N*/10-hydrochloric acid for 10 c.c. of protein solution) at which the protein coagulated most rapidly on heating. The above experiments were repeated with such a protein mixture, but again there was no difference between *ac* and *b*.

Finally, the protein was finely dispersed by the addition of sodium hydroxide (1 c.c. of *N*/10-solution to 10 c.c. of protein solution), and the mixture with methylene-blue examined in the usual way, the comparison liquid being a solution of sodium hydroxide of the same  $p_H$  as the protein mixture. No adsorption of methylene-blue was detected.

*Casein*.—A solution of 2 g. of casein (Hammersten) in 60 c.c. of water and 2 c.c. of *N*-sodium hydroxide was diluted to 100 c.c. with water, a slight excess of hydrochloric acid added, and the solution kept for 12 hours. The precipitated casein was washed free from chloride, and dissolved in 100 c.c. of *M*/15-disodium hydrogen phosphate or *M*/15-sodium carbonate.

The  $p_H$  of the phosphate solution was 7.45. A buffer solution of the same  $p_H$  was made by mixing 84 c.c. of *M*/15-disodium hydrogen phosphate with 16 c.c. of water.

Mixtures of either solution of casein (phosphate or carbonate) with methylene-blue were examined, but no difference was found between *ac* and *b*, and therefore no adsorption occurred.

*Pure Albumin*.—A 10% solution of white of egg was mixed with an equal volume of saturated ammonium sulphate solution, the precipitated globulin removed, and the filtrate dialysed for several days until it was free from sulphate. The solution of albumin thus obtained was used in experiments with methylene-blue, but no adsorption was detected.

*Saponin*.—The transmission curve of a mixture of methylene-blue with a 10% solution of saponin (for which  $a = 1$ ) was the same as that of its mixture with water. There was, therefore, no adsorption.

Kobert (Freundlich, "Kapillarchemie," 3rd ed., 1923, p. 889) dialysed a saponin solution against a solution of methylene-blue and showed that the dye accumulated in the sol so that its concentration there exceeded that in the external solution. We tried to repeat this experiment; but the whole of the methylene-blue was adsorbed by our dialysis membrane ("Dialysierhülse" of Schleicher and Schüll) and both liquids became colourless.

*Gelatin*.—A 1% solution of gelatin, made by warming 1 g. to 70° with 100 g. of water, becomes more opalescent on standing, but if it is prepared under the proper conditions, reproducible values of its transmissive power can be obtained. The calculated and the experimental values of the transmissive power of the mixture methylene-blue + gelatin were the same. Hence gelatin does not adsorb the dye.

#### *Discussion.*

It has been shown that sols of proteins, such as casein, natural white of egg, purified albumin and gelatin, do not adsorb methylene-blue; the substances remain mutually uninfluenced. This result is very remarkable, because, in the precipitation of a solution of protein containing methylene-blue by means of electrolytes, the dye always comes down with the coagulum and colours it blue. Possibly in the latter case, the particles of protein may be completely dehydrated; and the activities of the hydrated and the dehydrated particles may be different.

Also aluminium hydroxide sol and methylene-blue in solution are without influence on each other. Flocculating aluminium hydroxide, however, may carry down methylene-blue. Since both substances are basic, the reason for the carrying down must be sought in some physical cause—an explanation which might be applicable to coagulating protein also. The conditions of this mechanical adsorption are of course not yet known. It must, however, be kept in mind that methylene-blue is mechanically retained by substances of many different kinds, *e.g.*, glass, filter-paper, different kinds of membranes, etc. The adsorption of methylene-blue by finely divided kaolin is also a mechanical one, as may be seen from the absorption curve. The experimental curve runs almost parallel to the calculated one and lies above it. Consequently the transmissive power observed is greater than that calculated, but here, unlike the case of silica sol or sodium silicate, no new absorption minimum results, so that there is no new specific absorption curve of the mixture to be observed. Indeed the calculated curve for the kaolin—

methylene-blue mixture has an absorption minimum, namely, that of pure methylene-blue, at  $\lambda = 637\mu$ , and this does not appear in the experimental curves for very low concentrations of methylene-blue (Table III). This, however, is because the kaolin adsorbs the whole of the methylene-blue.

The absorption curve of the system silica sol + methylene-blue, on the other hand, is characteristic in that it has a new absorption minimum (quite removed from that of the methylene-blue). This and the production of a violet colour, appreciable by the naked eye, indicate chemical combination between the silica and the dye.

The same violet coloration and the same absorption minimum are obtained when a dilute solution of water-glass mixed with methylene-blue is used. The same compound is produced with its own absorption minimum at  $\lambda = 590\mu$ , near which the absorption minimum of methylene-blue also is to be found.

This investigation shows that it is possible by spectrophotometric methods to determine (1) whether a dye is not adsorbed at all by colloidal adsorbents (*e.g.*, albumin, casein, gelatin,\* saponin, aluminium hydroxide sol), (2) whether a mechanical adsorption takes place, *e.g.*, kaolin suspension (*lyosorption*), or (3) whether there is chemical combination between the adsorbent and the dye, *e.g.*, water-glass solution, silica sol (*chemosorption*). (See Fodor, *Koll.-chem. Beih.*, 1923, 18, 77; "Grundlagen der Dispersoid Chemie," Dresden u. Leipzig, 1925.)

In case 1 the curves calculated from the values of  $a$  and  $c$  agree with the experimental curves.

In case 2 there is a parallel displacement upwards of the experimental curve.

In case 3 the curve has a special form with one (or perhaps several) new absorption minimum.

It is often very difficult to distinguish between chemosorption and lyosorption. In case 3, however, we believe that the appearance of a new absorption minimum indicates chemosorption. An example of the capacity of colloidal solutions to form reproducible definite stoichiometric compounds is to be found in the case of the albumin solutions investigated by Sørensen and Höyrup (*Z. physiol. Chem.*, 1918, 103, 104).

We have to thank Miss S. Rubinstein for help in the experimental part of the work.

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\* Recent researches have shown that the phospho-protein sol from yeast-macerate is able to fix methylene-blue fairly strongly. The results will be published later.



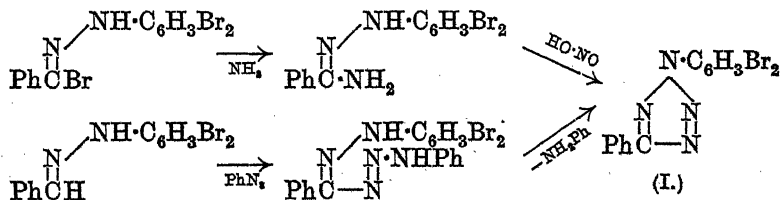
# XIX.—*Substituted Dihydropentazines—A New Series of Cyclic Nitrogen Compounds.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

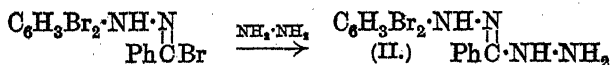
It has recently been shown (J., 1925, 127, 975, 1687) that when halogens react with benzaldehydephenylhydrazones substitution occurs in the hydrazine residue and in the so-called  $\omega$ -position, that is, in the  $\cdot\text{CH}\cdot$  group. This affords an easy method of obtaining in quantity many substituted hydrazones, in which the  $\omega$ -halogen is unusually reactive.

Such  $\omega$ -bromo-substituted hydrazones, for example, react with ammonia to form hydrazidines which are converted by the action of nitrous acid into tetrazoles (compare Pinner, *Ber.*, 1894, 27, 984).

Several tetrazoles, prepared by this method, which establishes their constitution, have been shown to be identical with the compounds produced by heating the corresponding hydrazone with phenyl azide (compare Dimroth, *Ber.*, 1910, 43, 2899). For example, benzaldehyde-2:4-dibromophenylhydrazone yields 1-(2:4-dibromophenyl)-4-phenyltetrazole by either method, thus:



These  $\omega$ -halogen compounds react also with hydrazine, replacing by a hydrazino-group, the  $\omega$ -halogen. For example,  $\omega$ -bromobenzaldehyde-2:4-dibromophenylhydrazone yields  $\omega$ -hydrazinobenzaldehyde-2:4-dibromophenylhydrazone\* (II):

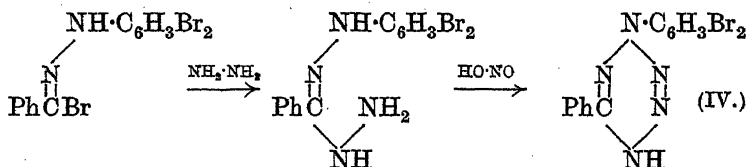


This compound behaves as a substituted hydrazine: it forms salts with halogen acids, yields an acetyl derivative when treated with acetyl chloride, and reacts with aldehydes, forming hydrazones. It also reacts with excess of  $\omega$ -bromobenzaldehyde-2:4-dibromophenylhydrazone, forming a compound having probably the constitution (III).



\* This behaviour is in marked contrast to that of phenylhydrazine, which converts the hydrazone into a formazyl compound (compare Pechmann, *Ber.*, 1894, 27, 322).

When treated with nitrous acid these  $\omega$ -hydrazinobenzaldehyde-hydrazone are converted into dihydropentazines. Thus, for example,  $\omega$ -hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone yields 1-(2 : 4-dibromophenyl)-5-phenyl-1 : 4-dihydropentazine (IV) :



The 5-phenyldihydropentazines are crystalline, odourless, weakly basic compounds which on being rapidly heated decompose, yielding benzonitrile.

#### EXPERIMENTAL.

*Preparation of 1-(2 : 4-Dibromophenyl)-4-phenyl-1 : 2 : 3 : 5-tetrazole (I).—*(a) *From  $\omega$ -bromobenzaldehyde-2 : 4-dibromophenylhydrazone.* The hydrazone was prepared by the action of bromine upon benzaldehydephenylhydrazone and converted into the corresponding hydrazidine by boiling with an aqueous alcoholic solution of ammonia (compare Chattaway and Walker, *loc. cit.*).

A suspension of finely ground benzaldehyde-2 : 4-dibromophenylhydrazidine (5 g.) in a mixture of 20 c.c. of concentrated hydrochloric acid and 10 c.c. of water was cooled in a freezing mixture and 1 g. of solid sodium nitrite was added very gradually with constant stirring. 1-(2 : 4-Dibromophenyl)-4-phenyltetrazole separated as a slightly brown solid. It was filtered off, washed repeatedly with water, and recrystallised from boiling alcohol, in which it is moderately easily soluble and from which it separates in a felted mass of fine, white needles, m. p. 127° (Found : Br, 41.7.  $\text{C}_{13}\text{H}_8\text{N}_4\text{Br}_2$  requires Br, 41.95%).

(b) *From benzaldehyde-2 : 4-dibromophenylhydrazone and phenyl azide.* A mixture of 5 g. of benzaldehyde-2 : 4-dibromophenylhydrazone, 2 g. of phenyl azide, and a solution of 0.4 g. of sodium in 8 c.c. of alcohol was heated at 100° in a sealed tube for 15 hours. The tetrazole which separated was filtered off, washed with a little alcohol, and recrystallised several times from boiling alcohol, separating as a felted mass of fine, white needles, m. p. 127°.

This and the tetrazole prepared by method (a) were identical in every respect.

1-(2 : 4-Dibromophenyl)-4-*m*-nitrophenyl-1 : 2 : 3 : 5-tetrazole (formula corresponding with I) was prepared similarly from  $\omega$ -bromo-*m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone. It separates from boiling alcohol, in which it is somewhat sparingly

soluble, in colourless needles, m. p.  $215^{\circ}$  (Found: C, 37.0; H, 1.7; N, 16.55; Br, 37.5.  $C_{13}H_7O_2N_5Br_2$  requires C, 36.7; H, 1.6; N, 16.5; Br, 37.65%).

*$\omega$ -Hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone* (II).—A suspension of 10 g. of finely divided  *$\omega$ -bromobenzaldehyde-2 : 4-dibromophenylhydrazone* in 50 c.c. of alcohol was added to 10 c.c. of a 50% hydrazine hydrate solution, and the mixture shaken vigorously for 15 minutes. It was then kept for 12 hours, when the whole had become a semi-solid, light brown mass. The solid was filtered off and the  *$\omega$ -hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone* separated from the hydrazine hydrobromide with which it was mixed, by heating it with 40–50 c.c. of alcohol and filtering hot. On cooling the warm alcoholic solution,  *$\omega$ -hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone* separated in almost colourless needles, m. p.  $123^{\circ}$  (decomp.) (Found: Br, 41.8.  $C_{13}H_{12}N_4Br_2$  requires Br, 41.7%).

This compound can be preserved unchanged for a considerable time in a sealed tube, although it darkens somewhat when exposed to light. When exposed to the air, it undergoes slow decomposition.

On adding excess of strong hydrochloric acid to a warm alcoholic solution of  *$\omega$ -hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone* the hydrochloride of the base separates on cooling as a colourless, microcrystalline powder, m. p.  $188^{\circ}$  (decomp.). The sulphate, obtained similarly, separates in minute, colourless plates which on heating decompose without melting.

*$\omega$ -Benzylidenehydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone*,  $C_6H_3Br_2 \cdot NH \cdot N : CPh \cdot NH \cdot N : CHPh$ , is obtained as a yellow, crystalline powder on warming together in alcoholic solution equivalent quantities of benzaldehyde and  *$\omega$ -hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone*. It separates from boiling alcohol, in which it is moderately easily soluble, in small, yellow needles, m. p.  $126^{\circ}$  (Found: Br, 33.8.  $C_{20}H_{16}N_4Br_2$  requires Br, 33.9%).

This compound dissolves with a yellow colour in strong alcoholic potash, and in strong sulphuric acid with a brown colour which soon changes to red.

*$\omega$ -p-Nitrobenzylidenehydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone*,  $C_6H_3Br_2 \cdot NH \cdot N : CPh \cdot NH \cdot N : CH \cdot C_6H_4 \cdot NO_2$ , was prepared similarly from *p*-nitrobenzaldehyde. It separates from boiling alcohol in small needles which appear dark violet by transmitted light and dark green by reflected light; m. p.  $194^{\circ}$  (Found: Br, 30.8.  $C_{20}H_{15}O_2N_5Br_2$  requires Br, 31.0%).

It dissolves in strong alcoholic potash with an intense blue colour, which fades almost immediately. With sulphuric acid a brown colour is produced which becomes violet on standing.

The action of a further quantity of  $\omega$ -bromobenzaldehyde-2:4-dibromophenylhydrazone upon  $\omega$ -hydrazinobenzaldehyde-2:4-dibromophenylhydrazone yields a compound, having in all probability the symmetrical constitution (III), *hydrazobenzaldehyde-2:4-dibromophenylhydrazone*.

This compound was obtained by boiling a solution of 2 g. of  $\omega$ -hydrazinobenzaldehyde-2:4-dibromophenylhydrazone and an equivalent quantity of  $\omega$ -bromobenzaldehyde-2:4-dibromophenylhydrazone in 20 c.c. of alcohol under reflux for 12 hours. A solid separated which was filtered off and recrystallised from boiling glacial acetic acid, in which it was fairly easily soluble and from which it separated in colourless needles, m. p.  $237^{\circ}$  (Found: Br, 43.2.  $C_{26}H_{20}N_6Br_4$  requires Br, 43.4%).

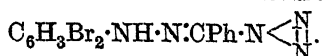
1-(2:4-Dibromophenyl)-5-phenyl-1:4-dihydropentazine (IV).—Five grams of finely divided  $\omega$ -hydrazinobenzaldehyde-2:4-dibromophenylhydrazone were added to a mixture of 25 c.c. of concentrated hydrochloric acid and 25 c.c. of water, and stirred vigorously. The hydrochloride of the base separated in the course of a few minutes as a finely divided, colourless, crystalline powder. The whole was then cooled in a freezing mixture and treated with 5 g. (a considerable excess) of sodium nitrite with constant stirring. The dihydropentazine separated as a pasty, slightly brown, semi-solid mass, which was filtered off and washed repeatedly with water. It was then washed with a little light petroleum (b. p.  $40-60^{\circ}$ ) and recrystallised from boiling alcohol, in which it is fairly easily soluble and from which it separates as a colourless, microcrystalline powder, m. p.  $172^{\circ}$  (decomp.) (Found: Br, 40.4; N, 17.6.  $C_{13}H_9N_5Br_2$  requires Br, 40.5; N, 17.7%).

When rapidly heated alone, the compound decomposes with a puff of black smoke and formation of benzonitrile. One g. of the substance was rapidly heated in a long glass tube sealed at one end. After decomposition drops of a yellow liquid condensed on the cool parts of the tube. The tube was washed out with ether, the ethereal solution filtered, and the ether evaporated. The residual drop of yellow oily liquid, which had a smell resembling that of benzonitrile, slowly dissolved when it was boiled with aqueous sodium hydroxide, ammonia being evolved; from the cooled, acidified solution, benzoic acid was obtained which separated from boiling water in white, shining flakes, m. p.  $120^{\circ}$ . The yellow oil was therefore benzonitrile.

1-(2:4-Dibromophenyl)-5-phenyldihydropentazine is a colourless, crystalline solid which exhibits slightly basic properties. It is without odour and is easily soluble in the common organic solvents. It is quite stable to air and light.

The action of nitrous acid on  $\omega$ -hydrazinobenzaldehyde-2:4-

dibromophenylhydrazone might conceivably have yielded, not the dihydropentazine, but an azide of the structure



That the compound produced has not this structure is shown by the circumstance that when heated at  $100^\circ$  for 60 hours in a sealed tube with acetone saturated with acetylene at  $0^\circ$  the whole was recovered completely unchanged. Had it possessed the azide structure it should have reacted with the acetylene, yielding 1:2:3-triazole-1-(benzaldehyde-2:4-dibromophenylhydrazone) (compare Dimroth, *Ber.*, 1910, 43, 2222). Further, as mentioned above, Pinner obtained phenyltetrazole and not benzenyliminoazide by the action of nitrous acid on benzenylhydrazidine,  $\text{NH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{NH}_2$ , which is an analogous compound to the  $\omega$ -hydrazino-compound from which the new ring compound was prepared. Its behaviour, therefore, is inconsistent with an azide structure, whilst it possesses the properties which would be expected in a dihydropentazine.

The formation of this compound is of considerable interest, as it contains a type of nitrogen ring apparently hitherto undescribed.

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[Received, December 1st, 1925.]

## XX.—*Purification of Phosphoric Oxide.*

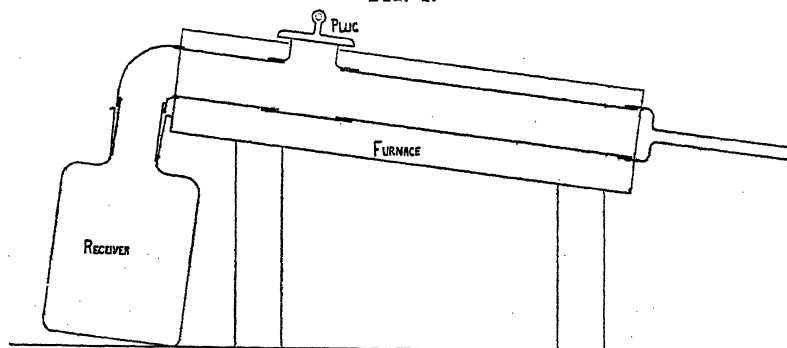
By GEORGE INGLE FINCH and REGINALD PERCY FRASER.

THE method for the purification of phosphoric oxide as devised by Finch and Peto (*J.*, 1922, 121, 692) has been employed in these laboratories for the last 4 years. In the light of the experience thus gained, several modifications in the original apparatus have been adopted which permit of the attaining of greater yields and increased rapidity of working. The modified form of apparatus consists of two iron tubes of 2-inch bore, the one 24 and the other 12 inches in length. These tubes are coaxially joined together by means of a  $2\frac{1}{4}$ -inch bore T-piece, the 1-inch long upper branch of which is machined flat and closed by the plug P, the lower surface of which is also machined. This 36-inch tube is supported in an inclined, gas-fired combustion furnace. Oxygen is led from a cylinder through glass wool into the lower end of the tube, the attachment being made by means of a length of  $\frac{1}{4}$ -inch iron tubing and a screwed adaptor. The cylinder oxygen employed in these laboratories is made by fractional distillation of liquid air and therefore needs no preliminary drying. The glass wool serves to retain dust. The upper and condensing end of the tube consists

of a  $2\frac{1}{4}$ -inch smoothly rounded, right angle bend, into the lower end of which a 2-inch length of 2-inch bore tubing is screwed. The receiver in which phosphoric oxide is condensed consists of a  $1\frac{1}{2}$  litre glass-stoppered bottle, the neck of which is just sufficiently wide to admit the 2-inch bore iron tube. The right angle bend as far as the neck of the bottle is well lagged with asbestos cloth and heated by means of a large T  clu burner in order to prevent condensation in the tube itself.

The method of operation is as follows. The main, 36-inch tube is first brought to a bright red heat. A rapid stream of oxygen (3 litres per minute) is then admitted, and 10 to 15 g. of the impure phosphoric oxide are fed in, in one lot, through the short branch of the T-piece into the main tube, whereupon the plug is immediately replaced. The viscous phosphoric acid soon formed on the

FIG. 1.



machined surfaces of the plug and T-piece forms an effective seal. Rapid volatilisation of the oxide occurs, and a dense white cloud of pure crystalline phosphoric oxide is seen to condense in the receiver. A fresh charge of impure oxide is introduced as soon as the condensation due to the previous charge subsides. Glassy phosphoric acids formed in the main tube flow down towards the oxygen inlet end. They may be removed when the tube is cold by unscrewing the  $\frac{1}{4}$ -inch adapter and hammering the tube. The necessity for this does not arise until after several pounds of oxide have been distilled. The 24-inch section of the main tube serves to preheat the oxygen and to distil the volatile portions of the viscous oxides. The distillation section of the main tube must be kept at a bright red heat, and the right angle bend and the short piece of tubing attached to it and entering the receiver must be kept at a sufficiently high temperature to prevent condensation anywhere in the iron tube itself. At a normal rate of working,

about 500 g. of oxide can be distilled in this manner in 1 hour. The yield obtained varied from 70 to more than 80%, according to the nature of the original impure oxide and the skill of the operator. Owing to the rapid rate and the high temperature (above  $800^{\circ}$ ) at which distillation occurs, a uniform crystalline product of a volume about 5 times that of the original oxide, and thus well suited for drying operations, is obtained. In order to obtain rapidly a good yield of pure product, distillation should not be commenced until the main tube is at a bright red heat with a large excess of oxygen passing through it. The receiver serves as the storage bottle, the stopper being lubricated with phosphoric oxide. The pure product obtained and stored in this manner will keep indefinitely.

The suitability of a phosphoric oxide for use in the experimental study of heterogeneous gas reactions or the attainment of a Bakerian degree of dryness depends on its vapour pressure, voluminous nature, and freedom from impurities, such as lower oxides of phosphorus and traces of organic matter. Smits and Rutgers (J., 1924, **125**, 2573) have shown that heating at temperatures above  $400^{\circ}$  yields that form of phosphoric oxide which exhibits the minimum vapour pressure. The rapid distillation carried out in the manner described above yields a crystalline product of great voluminousness. Traces of organic impurities may be detected by gently heating the moistened product in a test-tube; discoloration occurs if organic matter is present. The absence of lower oxides of phosphorus is best confirmed by the silver nitrate test described by Finch and Peto (*loc. cit.*). The mercuric chloride test also mentioned by them and advocated by Whitaker (J., 1925, **127**, 2219) has been found by us to be less sensitive than the silver nitrate test and therefore is not to be recommended.

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## XXI.—*Production of Arsenic Subsulphide. Reduction of Certain Arsenic Compounds by Sodium Hyposulphite [Hydrosulphite].*

By WALTER FARMER and JAMES BRIERLEY FIRTH.

PRELIMINARY experiments on the reduction of certain arsenic compounds by sodium hyposulphite gave a product which was insoluble in colourless ammonium sulphide and appeared to be a subsulphide of arsenic. In the present investigation the pro-

ducts obtained by reducing various arsenic compounds in acid and in alkaline solution by sodium hyposulphite were examined.

In all the experiments the amounts of the different arsenic compounds taken were equivalent to the quantity of arsenic contained in 1 g. of pure arsenic trioxide, *i.e.*, 0.7575 g. of arsenic.

Filtration and washing of the precipitate at room temperature was a very slow process; if, however, the product was heated to boiling, the precipitate coagulated, and filtration and washing were greatly facilitated; also analysis showed that the composition of the precipitate was not affected by this treatment.

*Analysis of the Product.*—A solution of the precipitate was obtained by two distinct methods: (a) oxidation by fuming nitric acid, (b) oxidation by sodium peroxide in presence of hydrogen peroxide. Both methods were used for the precipitate obtained in each experiment and the two sets of results obtained showed satisfactory agreement. In each case, the arsenic was estimated as magnesium pyroarsenate (Levol, see Treadwell's "Analytical Chemistry," 1915, Vol. ii, pp. 206—208) and the sulphur as sulphate (Hentz and Weber; *op. cit.*, p. 469). To obtain a further check on the results, the arsenic remaining in the filtrate and washings was also estimated.

*Series I. Reduction (a) at 18°, (b) at 0° in Hydrochloric Acid of Definite Concentration by Sodium Hyposulphite in Various Concentrations.*—The requisite quantity of the arsenic compound was dissolved, if necessary by heating under reflux, in a mixture of 5 c.c. of concentrated hydrochloric acid and 45 c.c. of water. A solution of the requisite quantity of sodium hyposulphite in 50 c.c. of water was rapidly added, making the total volume 100 c.c. In all cases there was an immediate precipitation of a dark brown product, the quantity of which varied with the concentration of hyposulphite used.

Experiments carried out over periods ranging from 30 minutes to 12 hours showed that the duration of the experiment did not appear to affect the nature of the decomposition product, but only slightly increased the amount of the precipitate. In all subsequent experiments, therefore, the reaction was allowed to proceed for 12 hours, the reaction flask being well stoppered and the contents frequently shaken. After 12 hours, the reaction products were heated just to boiling point, and the precipitate was filtered off, thoroughly washed, dried at 100°, and weighed. In series (b), the solutions were cooled to 0° before mixing and the temperature of the mixed solutions was maintained at 0° for 12 hours. The results are in Table I; *w* = grams of hyposulphite in 100 c.c. of mixed solutions.



TABLE I.

As compd.	w.	(a) Reaction temp. 18°.			(b) Reaction temp. 0°.		
		% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
As <sub>2</sub> O <sub>3</sub>	4	64.19	86.69	13.47	61.25	87.50	12.68
	6	68.74	85.63	14.51	65.39	86.38	13.78
	8	73.09	85.92	15.25	69.98	85.80	14.33
	10	79.12	84.03	16.09	75.26	84.87	15.28
As <sub>2</sub> O <sub>5</sub>	4	36.34	75.79	24.35	35.61	85.87	14.30
	6	37.20	74.87	25.25	36.75	85.13	15.01
	8	38.98	74.02	26.08	37.98	84.50	15.68
	10	40.05	73.41	26.75	39.78	83.81	16.31

*Series II. Reduction at 18° in Oxalic Acid Solution of Definite Concentration by Various Amounts of Sodium Hyposulphite.*—This series was carried out in order (if possible) to reduce the rate of decomposition of the sodium hyposulphite in the acid solution. The requisite quantity of the arsenic compound (= 0.7575 As) was dissolved in a solution of 4.5 g. of oxalic acid in 75 c.c. of water. The hyposulphite was dissolved in 25 c.c. of water and rapidly added to the oxalic acid solution. Other details were as before. The results are in Table II.

TABLE II.

w.	As <sub>2</sub> O <sub>3</sub> .			As <sub>2</sub> O <sub>5</sub> .		
	% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
4	73.20	80.31	19.86	36.19	75.89	24.25
6	87.22	76.91	23.24	37.45	75.12	25.03
8	88.53	76.33	23.86	38.97	74.55	25.56
10	90.89	75.89	24.31	40.11	74.23	25.93

*Series III. Reduction at 18° in Hydrochloric Acid of Various Concentrations by Sodium Hyposulphite of Definite Concentration.*—In order to ascertain the effect of acid concentration, solutions of 1 g. of arsenic trioxide in 50 c.c. of hydrochloric acid of definite strength were each treated with 25 c.c. of a solution containing 10 g. of sodium hyposulphite. With increasing concentration of acid the colour changed from dark brown to very light brown. The results are in Table IIIa. This series was repeated, a quartz vessel being used. The results are in Table IIIb.

TABLE III.

As compd.	C.c. of conc. HCl.	% As ppted.		% As in ppte.		% S in ppte.	
		a.	b.	a.	b.	a.	b.
As <sub>2</sub> O <sub>3</sub>	5	87.16	82.19	85.69	80.82	14.49	19.46
	10	84.26	78.65	80.96	73.78	19.25	26.47
	20	79.42	76.98	73.48	69.48	26.71	30.83
	30	74.95	71.89	62.77	59.56	37.39	43.73
	40	72.91	70.05	56.22	53.60	43.98	46.76

*Series IV. Reduction in Potassium Hydroxide Solution of Definite Concentration by Sodium Hyposulphite in Various Concentrations.*—Preliminary experiments showed that no dark brown precipitates were formed at room temperature, even after 3 hours. As the temperature was being raised to the boiling point of the alkaline solution in which the reduction was taking place, there was a continuous darkening of the reaction liquid followed by the formation of a dark brown precipitate, the bulk of which increased after the liquid had reached the boiling point. The escaping vapour contained a gas having a strong garlic odour. This gas was further examined. The flask containing the reaction liquid was fitted with a small reflux condenser, to the top of which a hard glass tube was attached. The reaction liquid was boiled for 30 minutes while one part of the tube was strongly heated. A white, crystalline sublimate of arsenious oxide and a metallic mirror of arsenic formed in the cooler parts of the tube. Further, the gas produced a black deposit of metallic silver in a dilute solution of silver nitrate and reacted with iodine in solution.

The subsequent experiments were carried out at the temperature of the boiling solution. A solution of the arsenic compound in 50 c.c. of 3*N*-potassium hydroxide was treated rapidly with the required amount of sodium hyposulphite dissolved in 50 c.c. of 3*N*-potassium hydroxide. The gas evolved from the boiling mixture was passed into 25 c.c. of *N*/10-iodine solution, the evolution being complete after 20 minutes. In subsequent experiments, therefore, the reaction liquid was maintained at the boiling point for 30 minutes, and was then diluted to 200 c.c. and filtered through a tared filter; the precipitate was thoroughly washed, dried, and analysed. The iodine solution was titrated with *N*/10-thiosulphate. The results are in Table IV.

TABLE IV.

As compd.	w.	% As ppted.	% As in ppte.	% S in ppte.	% As evolved.
As <sub>2</sub> O <sub>3</sub>	4	77.02	95.84	4.30	0.50
	6	79.75	95.68	4.49	0.50
	8	83.20	93.50	6.65	0.50
	10	86.66	89.02	11.16	0.49
As <sub>2</sub> O <sub>5</sub>	4	trace	—	—	0.40
	6	trace	—	—	0.40
	8	5.93	92.19	8.06	0.42
	10	8.38	90.09	10.08	0.42

*Series V. Reduction at 18°, a Neutralisation Method being used in which the Arsenic Compound dissolved in Hydrochloric Acid of Definite Volume and Concentration is reduced by Various Amounts of Sodium Hyposulphite dissolved in Potassium Hydroxide Solution of the same Volume and Normality as the Hydrochloric Acid.*—The

hyposulphite dissolved in 50 c.c. of 1.2*N*-potassium hydroxide was rapidly added to a solution of the arsenic compound in 50 c.c. of 1.2*N*-hydrochloric acid. In all cases, there was an immediate precipitation of a dark brown substance; after 12 hours, this was filtered off, washed, dried, weighed, and analysed. The results are in Table V.

TABLE V.

w.	Arsenic trioxide.			Trisodium arsenite.		
	% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
4	82.75	93.18	6.96	69.79	88.09	13.12
6	88.37	93.47	6.70	76.02	88.15	13.08
8	94.81	93.62	6.57	80.05	88.21	13.02
10	99.24	93.89	6.24	87.28	88.17	13.06

	Arsenic pentoxide.			Trisodium arsenate.		
	% As	% As in	% S in	% As	% As in	% S in
4	50.08	76.89	23.29	40.39	69.31	30.88
6	51.98	76.42	23.72	42.56	69.17	30.97
8	55.13	75.93	24.22	43.97	68.88	31.28
10	57.25	75.73	24.46	45.48	68.77	32.41

With the exception of this series (V), the results obtained with trisodium and tripotassium arsenites and arsenates were similar to those obtained with the trioxide and pentoxide respectively.

*Further Examination of the Precipitates.*—The precipitates obtained in the foregoing experiments were repeatedly digested with colourless ammonium sulphide until on acidifying the extract no precipitate of arsenic sulphide was obtained.

With the exception of those obtained in the experiments in alkaline solution, the precipitates contained 6, 12, 25, or 32% of sulphur. A few contained 40% or more, and some were of intermediate composition.

Products of similar composition gave similar results when digested with colourless ammonium sulphide. The following are typical examples. In the fifth experiment there was, after digestion, a very small, dark brown residue containing arsenic and sulphur.

TABLE VI.

Original As compd.	Exptl. condition as in series.	Comp. before digestion.		Comp. after digestion.		Time of digestion (days).
		% As.	% S.	% As.	% S.	
As <sub>2</sub> O <sub>3</sub>	I (a)	85.63	14.51	77.38	12.69	5
As <sub>2</sub> O <sub>5</sub>	I (b)	83.81	16.31	77.33	12.71	5
As <sub>2</sub> O <sub>3</sub>	II	80.31	19.86	77.35	12.68	7
As <sub>2</sub> O <sub>5</sub>	II	74.23	25.93	77.31	12.75	7
As <sub>2</sub> O <sub>3</sub>	III	56.22	43.98	—	—	10
As <sub>2</sub> O <sub>5</sub>	IV	95.84	4.30	96.11	3.92	7
As <sub>2</sub> O <sub>5</sub>	V	90.19	9.98	94.87	5.22	7
Na <sub>2</sub> AsO <sub>4</sub>	V	68.81	31.41	71.17	25.89	3
				77.41	12.81	10

The average sulphur content of the residues after extraction was 12.69% in the case of the precipitates containing initially 12.5 to 32.5% of sulphur. As  $\text{As}_2\text{S}_3$  requires S, 12.45%, the final product would appear to be this subsulphide, the slightly high value for sulphur being due to retention of a little arsenious sulphide, the removal of the last traces of which is very difficult. For those precipitates containing less than 12% of sulphur, the results were not so consistent; e.g., for the final product from arsenic trioxide treated by the neutralisation method the mean sulphur content after extraction was 4.8%, whilst the precipitates from alkaline solutions gave final products containing 2.5 to 5.35% of sulphur.

#### *Discussion and Conclusions.*

One of the products of reduction of the arsenic compounds used is a sulphide of arsenic which contains about 12.7% of sulphur and is insoluble in colourless ammonium sulphide. It agrees in composition with the subsulphide of arsenic  $\text{As}_2\text{S}_3$  and appears to be identical with the substance obtained by Scott (J., 1900, 77, 651) by treating an aqueous solution of an alkali arsenate with phosphorus trichloride and saturating the mixture with sulphur dioxide. Products containing from 2.5 to 5.35% of sulphur have also been isolated.

In moderately acid solutions trivalent arsenic compounds yield precipitates of arsenic subsulphide,  $\text{As}_2\text{S}_3$ , containing comparatively small quantities of arsenic trisulphide, whilst quinquivalent arsenic compounds yield precipitates which approximate in composition to the formula  $\text{As}_2\text{S}_3 \cdot \text{As}_2\text{S}_5$  (25.42% S). The total arsenic precipitated from the latter compounds is approximately half that from the former.

Similar results are obtained by the neutralisation method, except that the precipitates from arsenic trioxide contain 6–7%, and those from alkali arsenates 30–32%, of sulphur ( $2\text{As}_2\text{S}_3 \cdot \text{As}_2\text{S}_5$  requires S, 29.89%).

Increase in acid concentration increases the amount of arsenic precipitated as trisulphide, and in strongly acid solutions the precipitate is mainly the trisulphide.

In alkaline solution, precipitation occurs not at room temperature but at the boiling point of the mixed solutions. In the case of arsenic trioxide the products contain 4–11% of sulphur. Arsenic pentoxide gives a comparatively small precipitate. A small amount of arsenic is volatilised at the boiling point of the mixture, mainly as trioxide associated with the hydride. The total arsenic precipitated increases, but not proportionally, with the concentration of the hyposulphite.

It would appear from the results that the subsulphide is formed by reaction between the tervalent arsenic compound and the hyposulphite, whilst the trisulphide is produced by the interaction of the arsenic compounds with thiosulphate and other thio-decomposition products of the hyposulphite. A yellow precipitate of arsenic sulphide is obtained when a solution of sodium thiosulphate containing alkali arsenite is acidified with hydrochloric acid and warmed. Hence increased concentration of hydrochloric acid increases the rate of decomposition of the hyposulphite, and the quantity of subsulphide produced is diminished and that of the trisulphide increased.

In the case of quinquevalent arsenic compounds, reduction to the tervalent compound first takes place with the production of thio-decomposition products; the arsenic is subsequently precipitated, partly as subsulphide by the hyposulphite and partly as trisulphide by the thiosulphate, etc.

At 0° (Series Ib), the sulphur content is diminished owing to the diminution in the rate of decomposition of the hyposulphite.

In no case was the arsenic completely precipitated from solution, but in neutral solution, with 10 g. of hyposulphite for 1 g. of arsenic trioxide, 99.24% (Series V) was precipitated. The maximum precipitation of arsenic from quinquevalent compounds was 57.25%, obtained in the same series under similar conditions.

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## XXII.—*Hydrogen Electrode Studies of the Precipitation of Basic Chromates, Borates and Carbonates.*

By HUBERT THOMAS STANLEY BRITTON.

THE work described in earlier papers (J., 1925, 127, 2110, 2120, 2142, 2148) showed that a characteristic property of a metallic hydroxide is the hydron concentration at which it separates from solution. The following electrometric titrations have therefore been carried out to see if the hydrogen-ion concentrations at which various basic precipitates are formed could in any way be correlated with the hydron concentrations at which the respective hydroxides are precipitated.

### I. *Basic Chromates.*

These titrations were made at 18° by the method used in the hydroxide investigations (*loc. cit.*) and chromic acid titration (Britton, J., 1924, 125, 1572). In Table I are the particulars of the solutions and the  $p_H$ 's at which precipitation took place.

TABLE I.

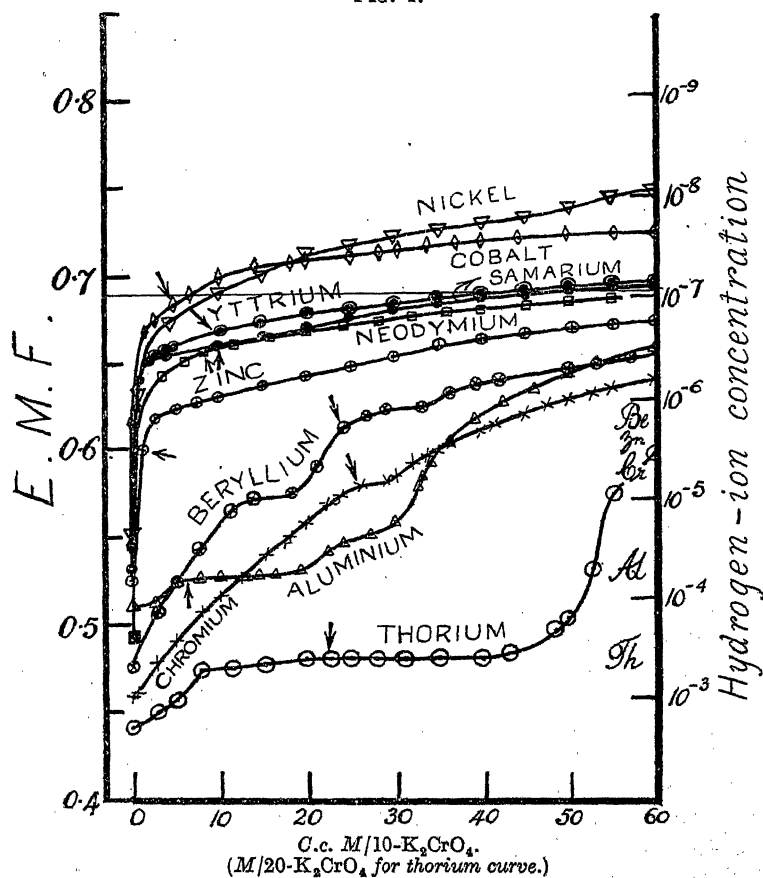
Solution (100 c.c.).	Ption of basic chromate began.		Ption of hydroxide began.		Ption.
	<i>E.M.F.</i>	<i>p<sub>H</sub></i>	<i>E.M.F.</i>	<i>p<sub>H</sub></i>	
0.01 <i>M</i> -ThCl <sub>4</sub>	0.482	3.45	0.484	3.51	Complete
0.00667 <i>M</i> -Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.524	4.18	0.521	4.14	"
0.01 <i>M</i> -Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·K <sub>2</sub> SO <sub>4</sub>	0.583	5.20	0.591	5.34	"
0.02 <i>M</i> -BeSO <sub>4</sub>	0.613	5.72	0.610	5.69	"
0.025 <i>M</i> -ZnSO <sub>4</sub>	0.600	5.49	0.583	5.20	
0.0132 <i>M</i> -Nd(NO <sub>3</sub> ) <sub>3</sub>	0.657	6.48	0.686	7.00	Partial
0.0133 <i>M</i> -SnCl <sub>2</sub>	0.661	6.55	0.676	6.83	"
0.0133 <i>M</i> -YCl <sub>3</sub>	0.672	6.74	0.674	6.78	"
0.0247 <i>M</i> -CoCl <sub>2</sub>	0.688	7.01	0.676	6.81	"
0.0200 <i>M</i> -NiCl <sub>2</sub>	0.674	6.78	0.666	6.66	'Opalescence

*M*/10-Potassium chromate was used in each titration except that of thorium chloride, in which case the concentration was *M*/20. The data relating to the different hydroxides were taken from the previous papers. The titration curves are given in Fig. 1, the arrows indicating the points at which precipitates first appeared.

*Mechanism of the Precipitation of Basic Chromates.*—Table I shows that in the majority of the titrations a precipitate did not form until the hydrogen-ion concentration of the solution had become that at which the hydroxide separates. In one or two cases the precipitate first formed was the hydroxide uncontaminated with any chromate. This was particularly the case with aluminium, the initial precipitate being aluminium hydroxide containing some unattacked sulphate. The chief factor controlling the concentration of hydrogen ions is the reaction whereby the acid, produced from the metallic salt by hydrolysis, and the potassium chromate generate hydrochromate ions. The dissociation of these ions is exceedingly small and is rendered still smaller by the increasing concentration of chromate ions from the added potassium chromate. The range of hydrogen-ion concentrations which can be produced in equilibria involving chromate and hydrochromate ions is  $10^{-5}$  to  $10^{-8}$ , as may be seen from the second section of the chromic acid titration curve (Britton, *loc. cit.*). For a considerable range of equilibria the hydrogen-ion concentration remains approximately  $10^{-6}$ . The reason why potassium chromate precipitates basic chromates from salt solutions lies in the inability of the hydrochromate ions to react with the metallic bases and thus maintain them in solution, except in the few instances in which insoluble normal chromates are formed. For example, consider the reactions between freshly precipitated aluminium hydroxide and the hydrochromate ions present in potassium dichromate solutions of different concentrations. It can be shown that the *p<sub>H</sub>* of *M*/10- and *M*/100-KHCrO<sub>4</sub> is 3.68 and 4.18 respectively, by assuming the salts to be completely dissociated into K<sup>+</sup> and HCrO<sub>4</sub><sup>-</sup>, and the latter ions to

be dissociated further into an equal number of hydrogen ions and chromate ions. As aluminium hydroxide is precipitated at  $p_H$  4.14, it follows that at the moment of formation of the precipitate the hydroxyl-ion concentration of the solution is  $K_w/10^{-4.14} = 10^{-10}$ . In order that the aluminium hydroxide may react with the hydrochromate ions and consequently dissolve, the hydrochromate ions

FIG. 1.



must be capable of providing sufficient hydrogen ions to form water with the hydroxyl ions in the solution, i.e., the product  $[H^+][OH^-]$  must be greater than  $K_w$ . If  $M/100$ -potassium hydrochromate solution be added to freshly precipitated aluminium hydroxide, it will set up a hydron concentration of  $10^{-4.18}$ , which, being less than the precipitation hydron concentration, will be incapable of causing solution, or, in other words,  $[H^+][OH^-]$  will become equal to  $10^{-14.18}$ ,

a value just less than  $K_w$ ,  $10^{-14.14}$ . With  $M/10$ - $\text{KHCrO}_4$ ,  $p_{\text{H}} = 3.68$ , the hydrogen-ion concentration will be less than that necessary for the precipitation of aluminium hydroxide and consequently there will be a tendency for the aluminium hydroxide to dissolve, the product being  $10^{-13.68}$ , which just exceeds the ionic product of water at  $18^\circ$ . If thorium hydroxide, however, be used, no reaction can take place, for its precipitation  $p_{\text{H}}$  being 3.5, the product of the hydroxyl-ion concentration and the hydron concentration arising from either  $M/10$ - or  $M/100$ -solution of the potassium acid chromate will be less than  $K_w$ .

The hydroxides higher in the  $p_{\text{H}}$  scale (*loc. cit.*, p. 2157) become increasingly reactive with the hydrochromate ions, though very little reaction takes place with those hydroxides which are precipitated from acid solutions. This is due to the fact that as soon as some hydrochromate ions have been converted into chromate ions, the hydrogen-ion concentration becomes considerably reduced and so prevents further reaction. As the hydron concentration thereby produced is about  $10^{-6}$ , its effect will be most marked with those hydroxides whose precipitation  $p_{\text{H}}$ 's are above 7. The reaction between those hydroxides, which are precipitated at  $p_{\text{H}}$  7 and above, and the hydrochromate radical becomes more pronounced and consequently potassium chromate causes either partial or no precipitation. Thus it is clear why potassium chromate fails to precipitate magnesium salt solutions. Magnesium hydroxide is precipitated at  $p_{\text{H}}$  10.5 and is therefore able to react with the ions produced in the second stage of the ionisation of chromic acid to an extent sufficient to prevent the attainment of the  $p_{\text{H}}$  of precipitation. Manganous hydroxide, too, is sufficiently strong ( $p_{\text{H}}$  8.4) to enter appreciably into combination with the hydrochromate radical. No precipitate is formed when potassium chromate is added to a manganous salt solution, but after some time the solution deepens in colour and eventually a brownish-black precipitate appears. This, however, is due to oxidation of the relatively large amount of manganous hydroxide present in the alkaline solution by the chromate and to some extent by the air (Gröger, *Z. anorg. Chem.*, 1905, 44, 453).

The latter precipitation reactions may also be considered from the point of view of the alkalinity of the potassium chromate solutions. By assuming complete ionisation of the various salts involved in the hydrolysis of potassium chromate solutions, it can be shown that at  $18^\circ$ ,  $[\text{H}^+] = \sqrt{K_2 K_w / C_{\text{K}_2\text{CrO}_4}}$ ,  $K_2$  of chromic acid being  $4.4 \times 10^{-7}$ . Therefore  $p_{\text{H}}$  of  $M/10$ -potassium chromate is 9.75 and of the  $M/100$ -solution, 9.25. Hence the addition of potassium chromate in either of these concentrations to mag-



nesium salt solutions cannot cause precipitation, as the reactants are incapable of attaining an alkalinity corresponding to the  $p_H$  of precipitation of magnesium hydroxide. On the other hand, it appears at first sight that if a dilute manganous salt solution contained (say)  $M/100$ -potassium chromate, the hydrogen-ion concentration which the latter would impart, *viz.*,  $10^{-9.25}$ , would be less than that at which manganous hydroxide is precipitated ( $p_H$  8.4). The reaction between manganous chloride (say) and potassium chromate involves a ready reaction between manganous hydroxide and the hydrions from the first stage of ionisation of chromic acid to form some  $Mn(HCrO_4)_2$  and also the more difficult reaction with the hydrions from the second stage. The result is that instead of the reaction being one of simple double decomposition, thus  $K_2CrO_4 + MnCl_2 = MnCrO_4 + 2KCl$ , the formation of a precipitate depends on how far the following equilibrium reaction is disturbed,  $Mn(HCrO_4)_2 + Mn(OH)_2 \rightleftharpoons 2MnCrO_4 + 2H_2O$ , which is governed, the oxidation effects which are peculiar to manganous and cobaltous hydroxides being excluded, by the two reactions (a)  $HCrO_4' + OH' \rightleftharpoons CrO_4'' + H_2O$ , and (b)  $Mn^{++} + 2OH' \rightleftharpoons Mn(OH)_2$ . Equilibrium (a) is dependent on  $K_2$  and  $K_w$ , and equilibrium (b) on  $[Mn^{++}][OH']^2$  or, more directly, the  $p_H$  of precipitation. Thus it follows that when  $M/10$ -potassium chromate is added to a manganous salt solution of the concentration used in these titrations, the  $p_H$  of the solution barely attains the precipitation  $p_H$  of manganous hydroxide and no precipitate is at first produced. More concentrated solutions of potassium chromate, however, effect partial but almost immediate precipitation of basic manganous chromate.

The behaviour of potassium chromate towards nickel and cobalt salt solutions is of interest. As shown in Table I, nickel hydroxide is precipitated at  $p_H$  6.66 and cobalt hydroxide at  $p_H$  6.81. Yet when  $M/10$ -potassium chromate is added to solutions of cobalt and nickel salts partial precipitation occurs in the former case and merely an opalescence is produced in the latter. The nickel and cobalt curves show that potassium chromate produces hydrion concentrations less than those at which the respective hydroxides are precipitated by alkali. The partial precipitation of cobalt is probably due to the tendency of cobalt hydroxide to oxidise. Gentle warming of the nickel solution is sufficient to cause precipitation.

The curves showing the course of precipitation of the basic chromates of neodymium and samarium have been included, for unlike the other metals except thorium, they form well-defined, difficultly soluble salts and thus the precipitation of one or the other

is determined by (a) the hydrogen-ion concentration and (b) the solubility of the normal chromate.

These hydrogen-ion relationships of the various hydroxides explain why solutions of potassium dichromate, in spite of their  $p_H$ 's being greater than the precipitation  $p_H$ 's of certain hydroxides, fail to cause the precipitation of basic chromates, except from zirconium salt solutions; and even in this case it is far from complete. Unless concentrated solutions be used, in which case the normal thorium chromate may be precipitated, the addition of potassium dichromate to thorium salt solutions fails to give a precipitate, although the  $p_H$  of the dichromate solution itself is greater (3.68—4.18 for solutions ranging from 0.1M to 0.01M) than the hydroxide precipitation  $p_H$ , 3.5. Potassium dichromate behaves, towards a weak base like thorium hydroxide, as a salt of a strong monobasic acid containing no reactive hydrogen atom, and on addition to a thorium salt solution merely sets up an equilibrium,  $\text{ThCl}_4 + 4\text{KHCrO}_4 \rightleftharpoons \text{Th}(\text{HCrO}_4)_4 + 4\text{KCl}$ , in which the thorium salt is largely hydrolysed, and thereby maintains a hydron concentration in the solution which is much greater than that required for the precipitation of the hydroxide. An excess of potassium dichromate will have a buffering effect on the hydrolysed chromic acid, but, as the first section of the chromic acid titration curve shows, the excess would have to be considerable before the hydrogen-ion concentration could be reduced to  $p_H$  3.5.

*Detailed Study of the Precipitation Reactions.—Thorium.* It was mentioned (J., 1923, 123, 1434) that when  $M/100$ -thorium nitrate solution was treated with  $M/20$ -potassium chromate solution in stoichiometrical amounts, precipitation was partial and the precipitate contained thoria and chromic anhydride in the molecular ratio 1:1.38. On substituting the chloride for the nitrate, no variation was found in the composition of the precipitate. Fig. 1 shows that 22.7 c.c. of  $M/20$ -potassium chromate caused the attainment of the hydroxide precipitation  $p_H$ , at which point basic thorium chromate began to be precipitated. The next 30 c.c. caused little change in  $p_H$ , but soon afterwards a rapid diminution in hydrogen-ion concentration occurred which marked the end of precipitation. On comparing the inflexion thereby produced with that in the neutralisation curve of chromic acid, it will be observed that it indicates the first half of the neutralisation of all the free chromic acid present in the solution,  $\text{KHCrO}_4$  being formed. The reaction may be regarded as two simultaneous reactions: first, the gradual hydrolysis of the thorium salt thus,  $\text{ThCl}_4 + 4\text{H}_2\text{O} \rightarrow \text{Th}(\text{OH})_4 + 4\text{HCl}$ , and, secondly,  $4\text{HCl} + 4\text{K}_2\text{CrO}_4 \rightarrow 4\text{KCl} + 4\text{KHCrO}_4$ .

As stated above, it would be expected that thorium hydroxide

would show a negligible tendency to react with the small concentrations of hydriions which arise from the dissociation of hydrochromate ions. Yet the thorium hydroxide which was precipitated contained appreciable amounts of chromic anhydride. Two reasons may be offered: (a) co-precipitation of thorium chromate, and (b) adsorption of chromic anhydride, through chemical forces at play between the weak base, thorium hydroxide, and the weak acid,  $\text{HCrO}_4'$ . The precipitates, apart from being yellow, resembled thorium hydroxide and appeared to contain no crystalline thorium chromate. Thorium chromate is much more soluble than the hydroxide, and seeing that the thorium- and chromate-ion concentrations were insufficient to produce a precipitate of the normal chromate before the hydroxide precipitation  $p_H$  was attained, it appears improbable that the basic chromate contained any normal chromate. The large chromic anhydride content of the basic precipitate was probably caused by a process akin to adsorption in which the chemical tendencies of the weak acid and the weak base played an important part.

An approximate estimate of the composition of the precipitate may be obtained from the titration curve. Precipitation was complete when 53 c.c. of  $M/20$ -potassium chromate had been added, i.e., an amount corresponding to the mid-point of the inflexion. If thorium hydroxide alone had been precipitated, then, as shown by the previous equations, 4 mols. of potassium chromate to 1 mol. of thorium chloride would have been required, or 80 c.c. in the titration; as compared with 2 mols., or 40 c.c. of  $M/20$ -potassium chromate, if the normal chromate had been formed. But actually 53 c.c. were required, and therefore by alligation the basic chromate precipitate must have contained  $27\text{Th}(\text{CrO}_4)_2, 13\text{Th}(\text{OH})_4$ , or  $\text{ThO}_2, 1.35\text{CrO}_3$ . The precipitate contained 54.55% of  $\text{ThO}_2$  and 28.47% of  $\text{CrO}_3$ , and therefore agreed with the formula  $\text{ThO}_2, 1.38\text{CrO}_3, 4.57\text{H}_2\text{O}$ , which is similar to that suggested by the curve.

*Aluminium.* Precipitation began when 5 c.c. of  $M/10$ -potassium chromate had been added, the  $p_H$  attained being that required for the precipitation of aluminium hydroxide. At first, the precipitate was white basic aluminium sulphate, but gradually became yellow and contained some chromate (compare Gröger, *Ber.*, 1902, 35, 3420). The curve shows that very little change in  $p_H$  ensued until 20 c.c. of potassium chromate had been added. The main inflexion occurred and precipitation became complete when between 32 and 35 c.c. were added. The precipitate was gelatinous and contained chromate, much of which could be removed by washing.

The experiments of Gröger on the solubility of aluminium hydroxide in chromic acid solutions throw some light on the reactivity

of the acid. He found that the number of molecules of chromic anhydride required to hold 1 mol. of alumina in solution varied from 4.46 to 5.02, and therefore concluded that both aluminium chromate and dichromate were capable of existence in solution. The explanation lies in the mode of dissociation of chromic acid. The first stage of the ionisation permits of the ready solution of aluminium hydroxide, thus  $\text{Al}(\text{OH})_3 + 3\text{H}_2\text{CrO}_4 \rightleftharpoons \text{Al}(\text{HCrO}_4)_3 + 3\text{H}_2\text{O}$ , which requires 6 mols. of  $\text{CrO}_3$  to 1 mol. of  $\text{Al}_2\text{O}_3$ , but the amount of hydrions produced in the second stage of the dissociation will depend on the concentration of chromic acid used. If it be large, the great concentration of hydrochromate ions will tend to suppress the second stage of dissociation and consequently there will be proportionally fewer hydrions available for reaction than in a more dilute solution. Hence it is clear why Gröger required variable amounts of chromic acid which corresponded to somewhat less than 6 mols.

*Chromium.* Maus (*Pogg. Annalen*, 1827, 9, 127) and later Storer and Eliot (*Proc. Amer. Acad. Arts Sci.*, 1862, 5, 192) found that brown precipitates of basic chromium chromate were produced by the action of potassium chromate on solutions of chromium salts, from which the chromic acid could be removed by repeated washing. The latter investigators stated that the abstraction did not stop when the precipitate had attained any particular composition and, from an equation based on the molecular proportion of potassium chromate which they found necessary for precipitation, concluded that  $\text{CrO}_2$ , i.e.,  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$ , must have first been formed.

The titration curve shows that the factor which determined precipitation was the hydrogen-ion concentration, for when 26 c.c. of  $M/10$ -potassium chromate had been added and the  $p_{\text{H}}$  had become 5.2, as compared with 5.34 found for the hydroxide, the basic chromate began to separate. The amount of potassium chromate required was 2.6 mols. to 1 mol. of chromic sulphate, and thus happens to be about half the quantity (5 mols.) found by Storer and Eliot. As the point of precipitation is determined by the hydrion concentration, the amount of potassium chromate required appears to be a function of the concentration of the reactants. The  $p_{\text{H}}$  change prior to precipitation was indicated by a line which was nearly straight, comparable with the section, corresponding to the addition of the first equivalent (to 1 Cr) of sodium hydroxide, in the alkali titration curve (*loc. cit.*). The fact that 2 mols. of sodium hydroxide had to be added to 1 mol. of chromium sulphate before precipitation began was due to the peculiar property of trivalent chromium of forming "soluble basic salts," such that in a solution of the sulphate one molecule of sulphuric acid is in a state

of loose combination which may perhaps be expressed by the equilibrium  $\text{Cr}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} \rightleftharpoons (\text{OH})_2\text{Cr}_2(\text{SO}_4)_2 \dots \text{H}_2\text{SO}_4$ , the looseness of the combination being indicated by the dotted line. This molecule of sulphuric acid, on its gradual release, reacted with two molecules of potassium chromate, thus:  $\text{H}_2\text{SO}_4 + 2\text{K}_2\text{CrO}_4 = 2\text{KHCrO}_4 + \text{K}_2\text{SO}_4$ , and the remaining 0.6 mol. of potassium chromate set up an equilibrium with the hydrochromate ions so formed to produce the requisite hydron concentration for precipitation.

The precipitates formed by treating chromium sulphate solution (alum) with varying proportions of potassium chromate, corresponding to 30, 60 and 90 c.c. in the titration, were analysed. After being freed from mother-liquor by suction and a little washing by decantation, the first precipitate was green and had the composition  $\text{Cr}_2\text{O}_3, 0.079\text{CrO}_3, x\text{H}_2\text{O}$ , and was thus almost pure chromium hydroxide; the second was brown and contained more chromate,  $\text{Cr}_2\text{O}_3, 0.574\text{CrO}_3, x\text{H}_2\text{O}$ ; and the third, still more, its composition being  $\text{Cr}_2\text{O}_3, 0.871\text{CrO}_3, x\text{H}_2\text{O}$ .

*Beryllium* is another of the elements that form soluble basic salts and this property appears to be reflected in the titration curve, the  $p_{\text{H}}$  at which precipitation began not being attained until 24 c.c. of  $M/10$ -potassium chromate had been added, i.e., 1.2 mols. for 1 mol. of beryllium sulphate.

The alkali curve (*loc. cit.*) shows a characteristic inflexion during the reaction with the first equivalent of sodium hydroxide; precipitation occurred at  $p_{\text{H}}$  5.69 (given at the top of an inflexion), when 1.04 equivalents had been added. A similar inflexion occurred in the chromate titration curve and precipitation began at  $p_{\text{H}}$  5.72, indicated by a point in a similar position. The equivalent amount of potassium chromate which produced this change was 2.4 times that of the alkali and consequently the change in hydron concentration was due to reaction between a loosely bound equivalent of acid in the beryllium sulphate molecule and potassium chromate, hydrochromate ions being formed which eventually entered into equilibrium with the added chromate ions.

Bleyer and Moorman (*Z. anorg. Chem.*, 1912, 76, 70; see also Orlov, *ibid.*, 1913, 79, 365) found that the interaction of potassium chromate and beryllium sulphate in solution produced very highly basic chromate precipitates, the chromate content of which seemed to increase slightly with the amount of potassium chromate added. Thus with 2 mols. of potassium chromate to one of beryllium sulphate the precipitate contained  $\text{BeO}, 0.036\text{CrO}_3$ , and with 4 mols. of potassium chromate,  $\text{BeO}, 0.07\text{CrO}_3$ , some unattacked sulphate being present in each precipitate. Bleyer and Moorman,

having found that chromic acid solutions saturated with beryllium hydroxide contained the two in equimolecular proportions, stated that beryllium chromate existed in solution. Solutions of strong acids saturated with beryllia are invariably basic, and, as shown by the titration curve of beryllium sulphate and sodium hydroxide (*loc. cit.*), the solution had to be rendered basic to an extent shown by the formula  $\text{Be}(\text{SO}_4)_{0.5}(\text{OH})$  before precipitation commenced. Similarly, the proportions in Bleyer and Moorman's solutions show that they were basic to the same extent, *viz.*,  $\text{Be}(\text{HCrO}_4)(\text{OH})$ , chromic acid being too weak in its second stage of dissociation to react with beryllium hydroxide to any appreciable extent.

*Zinc.* Table I shows that the  $p_{\text{H}}$  of precipitation of basic zinc chromate was 5.49 and therefore a little higher than that of the hydroxide, 5.20. The rapidity with which the  $p_{\text{H}}$  changed during the addition of the first c.c. of potassium chromate rendered it difficult to ascertain with any degree of precision the exact point at which the precipitate appeared. The precipitate was basic and consequently the hydron concentration of the solution was controlled mainly by the equilibrium between the liberated hydrochromate ions and chromate ions. Gröger's analyses (*Monatsh.*, 1904, 25, 520) showed that the precipitates obtained by treating zinc sulphate solutions with potassium chromate were indefinite and contained some sulphate, but the precipitates obtained from zinc chloride solutions were free from chloride, evidently due to the greater ease with which chlorides are hydrolysed. Varying amounts of potassium chromate were retained but were removable by washing.

An insoluble normal zinc chromate has been stated to exist by Schultze (*Z. anorg. Chem.*, 1895, 10, 148) and Briggs (*ibid.*, 1908, 56, 254), but the latter's data are unconvincing. It was thought that, if a difficultly soluble chromate did exist, its solubility might be too large for it to be precipitated by double decomposition through the attainment of the  $p_{\text{H}}$  at which the basic chromate separated, but that it might be precipitated from a chromic acid solution of zinc oxide by the gradual addition of potassium chromate so that the  $p_{\text{H}}$  should be kept below that necessary for the precipitation of the basic chromate (compare Britton, J., 1924, 125, 1875). Indefinite basic chromates were always obtained; *e.g.*, one air-dried precipitate,  $\text{ZnO}, 0.605\text{CrO}_3$ , contained 55.03% ZnO and 40.90%  $\text{CrO}_3$ , and another contained 58.10% ZnO and 33.00%  $\text{CrO}_3$ , corresponding to  $\text{ZnO}, 0.462\text{CrO}_3$ .

Some criticism appears to be necessary of Gröger's conclusions (*Z. anorg. Chem.*, 1911, 70, 135) from his study of the 25°-isotherm of the system  $\text{ZnO}-\text{CrO}_3-\text{H}_2\text{O}$ , in which he claims to have established

the identity of several definite basic chromates of zinc. The "rests" were considered, without experimental proof, to be the actual solid phases alone. If the molar concentrations of Gröger's liquid phases of ZnO be plotted against those of  $\text{CrO}_3$ , it will be found that all the points lie on a continuous curve, whereas had definite basic salts been formed the curve should display a number of "breaks," indicating the univariant points.

Although Gröger's conclusions can scarcely be regarded as valid, the analyses of his liquid phases are important in that they give the solubility of zinc oxide in chromic acid solutions varying in concentration from 0.006*M* to 9.7*M*, and therefore should give some idea of the reactivity of chromic acid towards zinc oxide. The number of molecules of chromic acid,  $\text{H}_2\text{CrO}_4$ , required to dissolve one molecule of zinc oxide varied continuously with increasing concentration of acid from 1.20 to 2.03, which led Gröger to conclude that the more dilute solutions contained both zinc chromate,  $\text{ZnCrO}_4$ , and zinc dichromate,  $\text{ZnCr}_2\text{O}_7$ , whilst the highly concentrated solutions contained only zinc dichromate. The fact that approximately two molecules of chromic acid were required for the most concentrated acid solutions was due to the reaction having taken place between zinc oxide and the hydrions of the first dissociation, thus:  $\text{ZnO} + 2\text{H}_2\text{CrO}_4 \rightarrow \text{Zn}(\text{HCrO}_4)_2 + \text{H}_2\text{O}$ , the large concentration of hydrochromate ions having inhibited further ionisation and consequent reaction, whereas in the dilute solutions some of the hydrions from the second stage of ionisation became available for reaction, with the result that less than 2 mols. of chromic acid were required.

*Cobalt and Nickel.* The reactions of these two metals have already been discussed (*vide supra*).

Reference may be made to Weil's proposal (*Bull. Soc. chim.*, 1911, 9, 20) to use potassium chromate for the separation of cobalt from nickel. Although potassium chromate does not precipitate basic nickel chromate at room temperature, the titration curve shows that the hydrion concentration produced by addition of potassium chromate to a nickel salt solution is such that the basic salt is on the point of being precipitated. A method depending on such a small difference in solubility can give but a rough separation, for there will be a great tendency for the gelatinous basic cobalt chromate to carry down much nickel.

*Rare Earths.—Yttrium.* Basic yttrium chromate began to be precipitated at the same  $p_x$  as its hydroxide, but precipitation was far from complete and the precipitate was highly basic. The air-dried precipitate formed by the interaction of stoichiometrical amounts of yttrium chloride and potassium chromate (40 c.c. of

$M/10\text{-K}_2\text{CrO}_4$  in the titration) solutions contained 38.61%  $\text{Y}_2\text{O}_3$  and 22.29%  $\text{CrO}_3$ , corresponding to the formula  $\text{Y}_2\text{O}_3 \cdot 1.30\text{CrO}_3$ . The filtrate from this precipitate was treated with more potassium chromate, and the new precipitate was still more basic and contained  $\text{Y}_2\text{O}_3 \cdot 0.93\text{CrO}_3$ .

*Neodymium and Samarium.* These two elements form well-defined but comparatively insoluble chromates (Britton, J., 1924, 125, 1875); the power of these earths to unite with chromic acid in its two stages being, no doubt, due to the small solubility of the salts formed, rather than to the strength of the bases. The solubilities of praseodymium chromate and lanthanum chromate are so small that when potassium chromate is added to the respective salt solutions the conditions requisite for the precipitation of the normal chromates are obtained before the hydroxide  $p_{\text{H}}$  is reached. This is not so with neodymium and samarium chromates, for they are sufficiently soluble to allow the  $p_{\text{H}}$  at which the hydroxide is precipitated to be attained before the respective solubility products of the chromates are exceeded, and consequently basic chromate precipitates are produced. When neodymium nitrate solution was treated with potassium chromate, a flocculent precipitate was obtained which on microscopic examination was seen to contain crystalline needles similar to those of the normal chromate. The following analyses refer to precipitates so obtained: (1)  $\text{Nd}_2\text{O}_3$ , 44.13;  $\text{CrO}_3$ , 34.59%, corresponding to  $\text{Nd}_2\text{O}_3 \cdot 2.64\text{CrO}_3 \cdot 9.02\text{H}_2\text{O}$ , and (2)  $\text{Nd}_2\text{O}_3$ , 47.95;  $\text{CrO}_3$ , 31.81%, corresponding to  $\text{Nd}_2\text{O}_3 \cdot 2.23\text{CrO}_3 \cdot 7.88\text{H}_2\text{O}$ . The fact that precipitation began at  $p_{\text{H}}$  6.48 instead of at 7.0, coupled with the nature of the precipitates and the relatively high  $\text{CrO}_3$  content, indicates that the formation of these precipitates constitutes a comparatively rare example of the co-precipitation of the crystalline normal salt and an indefinite basic salt.

Samarium chromate has a greater solubility than neodymium chromate and does not appear to be precipitated with the basic chromate. As the titration curve shows, the basic chromate was precipitated at  $p_{\text{H}}$  6.55, which was somewhat lower than the hydroxide  $p_{\text{H}}$ . It was yellow and flocculent and when dried and examined under the microscope appeared to be entirely amorphous. Its separation was partial. The air-dried precipitate from the titration contained 25.1%  $\text{CrO}_3$  as compared with 37.84% in  $\text{Sa}_2(\text{CrO}_4)_3 \cdot 8\text{H}_2\text{O}$ .

## II. Basic Borates.

Electrometric titrations were carried out at 18° with 0.05M-borax solution and salt solutions, which were so chosen that the precipitation reactions could be studied over as wide a range of hydrogen-



ion concentration as possible. Details of the solutions used and the  $p_H$ 's at which precipitates first appeared are in Table II.

TABLE II.

Solution (100 c.c. .	Ppton of basic borate began.		Ppton of hydroxide began.		Ppton.
	<i>E.M.F.</i>	$p_H$ .	<i>E.M.F.</i>	$p_H$ .	
0.01 <i>M</i> -ZrCl <sub>4</sub>	0.517	4.07	0.390	1.86	Complete
0.01 <i>M</i> -ThCl <sub>4</sub>	0.554	4.70	0.484	3.51	"
0.0067 <i>M</i> -Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.521	4.14	0.521	4.14	"
0.01 <i>M</i> -Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , K <sub>2</sub> SO <sub>4</sub>	0.586	5.25	0.591	5.34	"
0.02 <i>M</i> -BeSO <sub>4</sub>	0.613	5.72	0.610	5.69	"
0.02 <i>M</i> -ZnSO <sub>4</sub>	0.587	5.27	0.583	5.20	"
0.02 <i>M</i> -MnCl <sub>2</sub>	0.792	8.82	0.770*	8.43*	Partial
			0.794	8.85	
0.02 <i>M</i> -MgSO <sub>4</sub>	—	—	0.885	10.49	None

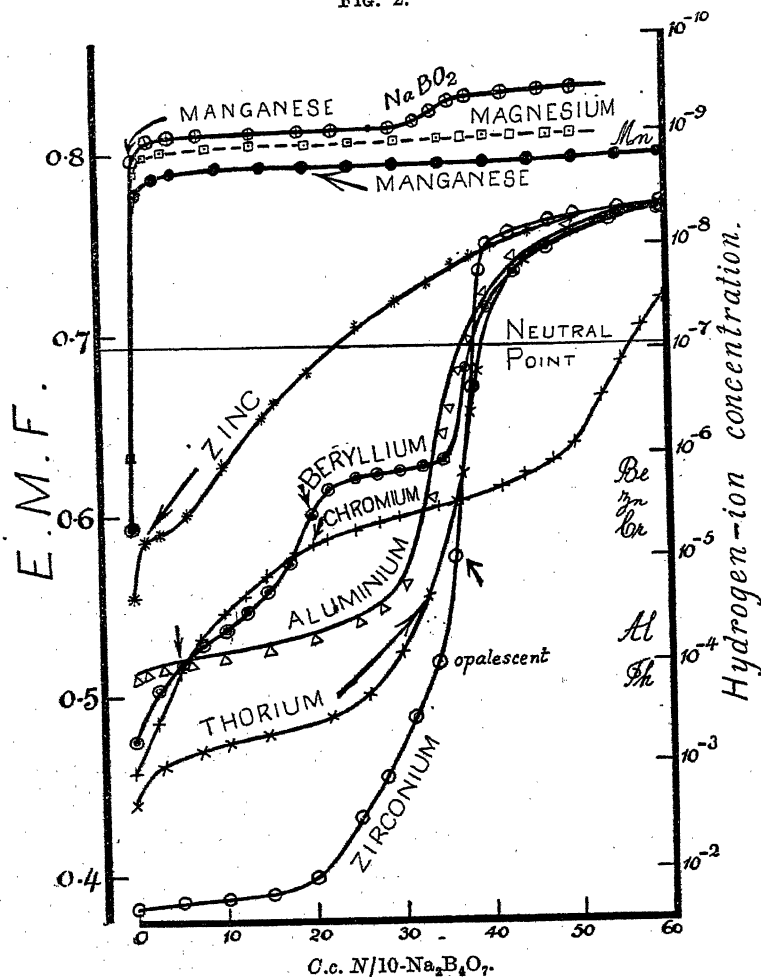
The titration curves are given in Fig. 2, the arrows showing the points at which precipitation began. The top curve in the diagram represents the titration of 100 c.c. of 0.02*M*-manganous chloride with 0.1018*M*-sodium metaborate.

Table II shows that, except in the case of zirconium and thorium, addition of borax solution did not cause precipitation to begin until the  $p_H$  at which the hydroxide is precipitated had been attained. The titration curves in Fig. 2, apart from that of zinc, are similar in shape to those representing the alkali titrations. Moreover, those curves which correspond to precipitation taking place in the acid zone show that the amounts of *N*/10-borax solution which caused the solutions to become alkaline, precipitation having become complete, were approximately the same as those required in the sodium hydroxide titrations. It appears, therefore, as far as the weaker bases are concerned, that sodium pyroborate has simply a hydrolysing action in precipitating the hydroxides, and in fact behaves as if no borate were present at all. The hydroxides which were precipitated contained some unattacked acid radical of the original salt, as may be seen from the amounts of *N*/10-borax required to render the solutions neutral, if it be assumed that the borate radical did not enter into combination. Thus in the zirconium titration, 38.5 c.c. were required as compared with the theoretical amount, 40 c.c.; thorium, 38.0 instead of 40 c.c.; aluminium, 36.0 instead of 40; chromium, 55 instead of 60; and beryllium, 37.6 instead of 40 c.c.

Provided that no insoluble normal borates are formed, it follows on theoretical grounds that boric acid, HBO<sub>2</sub>, with its exceptionally small dissociation constant, is incapable of producing hydrogen-ion concentrations large enough to cause dissolution of any of the hydroxides which are precipitated at  $p_H$  less than 7. As far as the reactivity of boric acid is concerned, boric acid behaves as a mono-

basic acid. If  $5 \times 10^{-10}$  be taken as an average value of  $K = [\text{H}^+][\text{BO}_2^-]/[\text{HBO}_2]$ , it follows that in a  $M/10$ -boric acid solution the hydrogen-ion concentration is  $10^{-5.2}$ , and  $10^{-5.6}$  in a  $M/100$ -solution. The hydroxides of beryllium, zinc, chromium, aluminium,

FIG. 2.



thorium and zirconium are all precipitated at  $p_{\text{H}}$  less than 5.69, and consequently the hydron concentrations of  $M/10$ - and  $M/100$ -solutions of boric acid are too small to have any solution effect on these hydroxides. Taking the case of beryllium hydroxide, which is precipitated at the highest  $p_{\text{H}}$  of the series under consideration,

in order that the reaction  $\text{Be}(\text{OH})_2 + 2\text{HBO}_2 \longrightarrow \text{Be}(\text{BO}_2)_2 + \text{H}_2\text{O}$  may proceed, water must be formed and therefore the product of the concentration of hydroxyl ions due to beryllium hydroxide, *viz.*,  $10^{-14.14}/10^{-5.69} = 10^{-8.45}$ , and that of the hydrions from the boric acid, about  $10^{-5.2}$ , must exceed  $K_w$ . In this case it is  $10^{-13.9}$ , and only just exceeds  $K_w$ , and consequently beryllium hydroxide may perhaps be expected to exhibit the slightest tendency to dissolve. Any solution, however, would cause an increase in the concentration of  $\text{BO}_2'$  ions, which would depress the ionisation of boric acid and so prevent further solution. Boric acid does not dissolve either of these bases to any appreciable extent.

The hydrogen-ion concentrations of the solutions at the end of these titrations were such as would be given by borate mixtures comprising the total quantity of boric acid added and the alkali in excess of that required for the precipitations, and therefore confirm the view that no boric acid, or relatively little, was contained in the precipitates. Thus in the titrations of zinc, beryllium, aluminium, thorium and zirconium, it will be seen from Fig. 2 that the hydrion concentration when 60 c.c. of *N*/10-borax had been added was  $10^{-8.3}$  in each case. By subtracting the 40 c.c. of *N*/10-sodium hydroxide which were neutralised during the precipitations, it is found that the solutions contained alkali equal to 20 c.c. of *N*/10-sodium hydroxide and boric acid equal to 120 c.c. of *N*/10- $\text{HBO}_2$ , the boric acid having been one-sixth neutralised. The  $p_H$  of a 0.2*N*-solution of boric acid neutralised to the same extent is, according to Sørensen, 8.29 (Prideaux, "Theory of Indicators," 1917, p. 279), and as the variation in  $p_H$  produced by the difference in concentration of the two solutions is very small, it will be seen that the agreement is sufficiently good.

Although the changes in hydrion concentration which took place in the acid zone of the titrations are almost identical with those which were obtained when the precipitant was sodium hydroxide, in the case of the weakest two bases, zirconia and thoria, the  $p_H$ 's of precipitation do not compare favourably with the corresponding hydroxide  $p_H$ 's. Zirconium hydroxide is generally precipitated at a  $p_H$  somewhere on the very slightly inclined part of the curve. In the precipitation of zirconium chloride solution with sodium hydroxide (J., 1925, 127, 2124) the  $p_H$  was 1.86, but in the present titration the solution remained perfectly clear until the inflexion in the curve had been passed and the  $p_H$  had become 4.06; opalescence then began. This was when 3.4 atoms of chloride of the zirconium tetrachloride had been replaced by hydroxyl groups and, notwithstanding its highly basic nature, the solution had remained perfectly clear. With thorium chloride, the effect was similar; the

solution remained quite clear until 3.3 atoms of chloride had been replaced and the curve had begun to incline, the  $p_H$  being 4.70 instead of 3.51 obtained by using alkali. Hence it appears that the boric acid was having some restrictive influence on the size of the particles. It is probable that the tendency, although very slight, which boric acid may have to combine with thorium and zirconia exerts its greatest influence just at the point where the hydroxide or basic salt is about to pass into colloidal solution prior to precipitation. If this be the case, it seems reasonable that the boric acid, in trying to react with the nascent hydroxide, tended to keep it in solution by impeding the growth of the particles. Two experiments were made to determine whether the delayed precipitation from a thorium chloride solution whose  $p_H$  is that at which precipitation normally takes place is a matter of time: To thorium chloride solutions of the concentration used in the titration were added amounts of borax equal to 2 and 3 equivalents; in neither case did a precipitate separate during a period of several weeks.

In the chromium titration, the solution became green on addition of the borax and precipitation occurred when 21.9 c.c. of  $N/10$ -solution had been added, or 1.09 equivalents for each atom of chromium.

The beryllium curve again is similar to the alkali curve, and precipitation was also delayed until 21.9 c.c. (= 1.09 equivalents to 1 atom of Be) had been added.

The zinc curve shows hydrogen-ion changes which were due mainly to equilibria which must have been set up between borate ions and boric acid. The precipitation  $p_H$  was the same as that when alkali was used.

The incomplete precipitation which took place from  $M/50$ -manganous chloride solution will be understood when it is remembered that the  $p_H$  of  $N/10$ -borax itself, viz., 9.11, is only slightly greater than the  $p_H$  at which manganous hydroxide is precipitated. Table II gives two  $p_H$  values for manganous hydroxide; the one marked with an asterisk is low, probably on account of oxidation of manganous hydroxide, and the other, which is approximately correct, was extrapolated from the alkali titration curve. In the borax titration the precipitate did not appear until 20 c.c. of  $N/10$ -borax had been added and  $p_H$  8.82 attained. The precipitate was white and remained dispersed until 50 c.c. had been added, and, unlike the hydroxide, it did not immediately turn brown through oxidation. It readily did so when washed. (It is this protective action which is conferred on manganous hydroxide by union with some boric acid which makes the substance of use as a "drier")

in paints and varnishes.) The fact that it was precipitated at the hydroxide  $p_H$  suggests that the white precipitate was basic, and not manganous borate as was stated by Hartley and Ramage (J., 1893, 63, 133). Their precipitates were obtained by pouring solutions of manganous sulphate into solutions of borax until no further precipitation occurred. From widely differing estimations of the manganese content only, they concluded that they had prepared a definite borate having the formula  $MnH_4(BO_3)_2$  when dried at  $100^\circ$ , and they state that  $MnH_2B_2O_5$  and  $Mn(BO_2)_2$  were formed by dehydrating it still more. They also state that manganous borate was produced by the interaction of manganous sulphate and sodium metaborate. The precipitate produced by the action of  $N/10$ -borax on  $M/50$ -manganous chloride solution was both indefinite and basic and contained  $MnO, 1.47HBO_2$ . In the titration of  $M/50$ -manganous chloride with  $0.1018N$ -sodium metaborate, the precipitate appeared when 1 c.c. of precipitant had been added and the  $p_H$  had become 8.77. This precipitate was, like the hydroxide, quickly oxidised and was strongly basic.

Laurent (*Comp. rend. Trav. Chim.*, 1850, 6, 33) observed that manganous salt solutions were not precipitated with potassium hexaborate. It will be seen from the hydrogen-ion concentrations of the various borate "buffer" mixtures that the  $p_H$  of a boric acid solution, a third of which has been neutralised with alkali and which thus corresponds to Laurent's reagent, is about 8.7; this falls just below the  $p_H$  at which the hydroxide is precipitated. When, however, the borate solution is added to a manganous salt solution, some of the alkali is neutralised and the  $p_H$  falls a little further below 8.7.

According to Gmelin-Kraut ("Handbuch anorg. Chem.," 1908, iii, [2], p. 324), Berzelius found that when a magnesium salt had been added to a manganous salt solution, borax failed to give a precipitate. Neutral salts, such as sodium chloride, sodium sulphate, calcium chloride and potassium chloride, also produce this effect, but to a lesser extent; e.g., a solution from which precipitation had been prevented with magnesium sulphate remained clear on standing, whereas by using either potassium chloride or any of the other salts brown precipitates appeared after 12 hours. Precipitates obtained by means of borax may be forced back into solution by the addition of these salts. Since the highest  $p_H$  that could be produced by borax solutions was far removed from the precipitation  $p_H$  of manganous hydroxide, it appeared that the behaviour of these salts in preventing precipitation of basic manganous borate lay in their power to diminish the  $p_H$  below that necessary for precipitation. For example, when 10 c.c. of a satur-

ated solution of magnesium sulphate were added to 100 c.c. of  $N/10$ -borax solution whose initial  $p_H$  was 9.11, the  $p_H$  fell to 8.58; with 40 c.c.,  $p_H$  was 8.10; and with 50 c.c., 8.06. The effect of potassium chloride was not so marked. The addition of much potassium chloride to a  $N/10$ -borax solution depressed the  $p_H$  only from 9.11 to 8.82—a value, it will be noticed, corresponding to incipient precipitation.

The dotted curve shows the changes produced in hydrogen-ion concentration during the addition of  $N/10$ -borax solution to a  $M/50$ -solution of magnesium sulphate. No precipitate was obtained, for the  $p_H$  of the borax solution was below that, 10.49, requisite for the precipitation of magnesium hydroxide. Borax produces in the boiling solution a precipitate which redissolves on cooling. No precipitate was obtained with  $N/10$ -sodium metaborate solution, for although its  $p_H$  was 10.85, the  $p_H$  of the mixture became a little lower than the necessary value.

### III. Basic Carbonates.

The hydrogen electrode titration method has been applied in a study of the relationships involved in the precipitation of basic carbonates. By using a plentiful supply of hydrogen electrodes which were efficient in ordinary solutions, potential differences between them and the normal calomel electrode were obtained, in these carbonate titrations, which were readily reproducible and were unaffected by any liberated carbon dioxide. Table III gives the particulars of the several titrations, and Fig. 3 shows the titration curves, the points at which precipitation began being again denoted by arrows. The sodium carbonate was decinormal in every case except the chromium titration, where it was 0.166*N*.

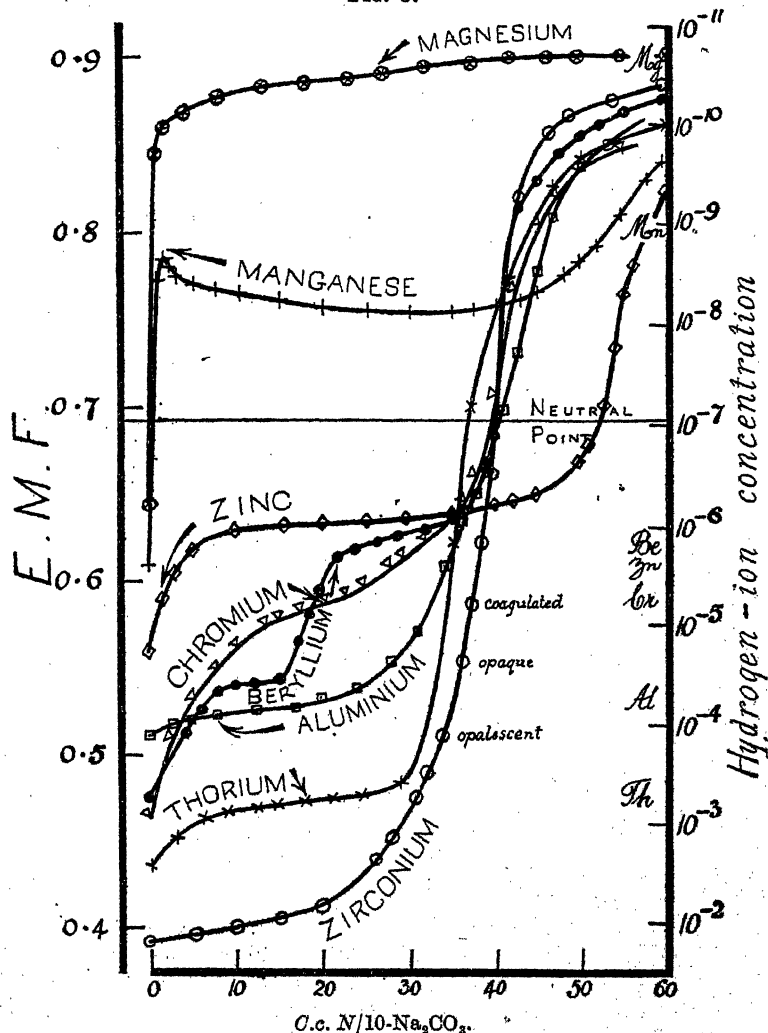
TABLE III.

Solution (100 c.c.).	Ption of basic carbonate began.		Ption of hydroxide began.		Ption. Complete
	<i>E.M.F.</i>	$p_H$ .	<i>E.M.F.</i>	$p_H$ .	
0.01 <i>M</i> -ZnCl <sub>2</sub>	0.511	3.95	0.390	1.86	
0.01 <i>M</i> -Th(NO <sub>3</sub> ) <sub>4</sub>	0.476	3.35	0.484	3.51	
0.0067 <i>M</i> -Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.523	4.16	0.521	4.14	"
0.01 <i>M</i> -Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·K <sub>2</sub> SO <sub>4</sub>	0.587	5.27	0.591	5.34	"
0.02 <i>M</i> -BeSO <sub>4</sub>	0.612	5.70	0.610	5.69	"
0.02 <i>M</i> -ZnSO <sub>4</sub>	0.589	5.30	0.583	5.20	"
0.02 <i>M</i> -MnCl <sub>2</sub>	0.784	8.68	0.794	8.85	"
0.02 <i>M</i> -MgSO <sub>4</sub>	0.891	10.54	0.885	10.49	Turbidity

The titration curves are of the same type as those obtained in the preceding hydrolytic precipitation titrations, and in every case but zirconium, precipitation began at hydron concentrations equal or very nearly equal to those necessary for the corresponding

hydroxides. *N*/10-Sodium carbonate, unlike the reagents used in the previous titrations, when added to the magnesium sulphate solution, produced an alkalinity corresponding, but only just so,

Fig. 3.



to the  $p_H$  at which the hydroxide is precipitated, which did not occur until 27 c.c. had been added. The precipitate formed even after 100 c.c. of sodium carbonate had been added did not amount to more than a slight turbidity.

The stoichiometrical quantity of sodium carbonate required for simple double decomposition was equivalent to 40 c.c. of  $N/10$ -sodium carbonate, except in the case of chromium, where it was 36 c.c. The curves for zirconium, thorium, aluminium, beryllium and chromium show that the mother-liquors became alkaline when approximately theoretical quantities of sodium carbonate had been added. The hydron concentrations at the end of the titrations, although differing somewhat owing to the escape of different amounts of carbon dioxide during the precipitations, were such as would be produced by mixtures of sodium bicarbonate and carbonate (compare Prideaux, "Theory of Indicators," p. 299; Auerbach and Pick, *Arb. K. Gesundheitsamt.*, 1911, **38**, 243). The changes in hydron concentration which took place during the precipitation of the basic carbonates from solutions whose hydrogen-ion concentrations were greater than  $10^{-6}$  were scarcely at all affected by the carbon dioxide that was liberated. The carbon dioxide set free during the precipitation of basic zinc carbonate, however, had so marked an effect on the hydrogen-ion concentration that the inflexion corresponding to the formation of sodium bicarbonate from the liberated carbon dioxide and the added sodium carbonate did not occur until 54 c.c. of the latter had been added.

The curve for manganese shows that the addition of  $N/10$ -sodium carbonate, after the first 2 c.c., produced a diminution in  $p_H$ , which reached a minimum, 8.2, when 30 c.c. had been added. The precipitate appeared when 1.4 c.c. had been added and  $p_H$  8.68, i.e., nearly the hydroxide  $p_H$ , had been attained. The precipitate first formed was basic, as may be seen from the curve, which shows that more than 40 c.c. of sodium carbonate had to be added before the  $p_H$  of sodium bicarbonate was attained, viz., 8.7.\* The precipitate, although basic, did not turn brown through oxidation by the air. It is remarkable that the increase in hydron concentration which occurred during the titration did not cause the basic carbonate to re-dissolve. This, however, was a case of two precipitations, one of the basic carbonate due to the  $p_H$ 's ruling at the beginning and at the end of the reaction, and the other of the normal carbonate, which was precipitated when the hydron concentration of the solution was enhanced. Sodium bicarbonate when added to a manganous chloride solution, preferably saturated with carbon dioxide, causes the precipitation of manganous carbonate only, for it cannot produce a sufficiently low hydron concentration to enable

\* It may be calculated from Noyes's formula (*Z. physikal. Chem.*, 1893, **11**, 495), by taking  $K_1$  and  $K_2$  of carbonic acid to be  $3 \times 10^{-7}$  and  $1.3 \times 10^{-13}$ , respectively, that the  $p_H$  of dilute solutions of sodium bicarbonate is about 8.7.



the basic carbonate to separate from solution; e.g., the hydron concentration of a manganous chloride solution was gradually reduced by the addition of a solution of sodium bicarbonate until  $p_H$  was 7.6; a white precipitate of manganous carbonate then began to form. Hence, in order to ensure the precipitation of the normal carbonate, the precipitant must be incapable of causing the  $p_H$  to be attained at which the hydroxide is precipitated.

Normal zinc carbonate has been prepared. The titration curve shows that in order to precipitate this salt uncontaminated with basic carbonate a reagent must be used which, besides causing the solubility product  $[Zn^{++}][CO_3^{--}]$  to be exceeded, will maintain a hydrogen-ion concentration greater than that at which the basic carbonate would separate. Sodium bicarbonate with its  $p_H$  of 8.7 would be useless, even though the carbon dioxide which would be set free during the precipitation would tend to increase the hydron concentration. It would be necessary to have the solution saturated with carbon dioxide under a very high pressure before any addition of sodium bicarbonate. Smith (*J. Amer. Chem. Soc.*, 1918, **40**, 883) has determined the solubility of zinc carbonate in solutions of carbon dioxide under pressures ranging from 4.12 to 40.6 atmospheres. His results may be used to calculate the hydrogen-ion concentrations of the various solutions which, being in equilibrium with zinc carbonate, were just on the point of precipitating zinc carbonate, if it be assumed, as was done by Bodländer (*Z. physikal. Chem.*, 1900, **35**, 23), that metallic bases exist in carbonic acid solutions in the form of bicarbonates. If zinc oxide exists as  $Zn(HCO_3)_2$ , the concentration of  $HCO_3'$  ions is equal to twice the concentration of dissolved zinc oxide, and, the extremely small concentration of hydrions arising from carbonic acid in its second stage of dissociation being neglected, it follows that  $[H^+] = [H_2CO_3]K_1/[HCO_3'] = ([CO_2] - 2[ZnO]) \cdot 3 \times 10^{-7}/2[ZnO]$ . It was thus calculated that the  $p_H$ 's of Smith's solutions varied continuously from 4.94 to 4.33. Even when the pressure of carbon dioxide is very high, the  $p_H$  at which the normal carbonate is precipitated is not very much less than that at which the hydroxide is precipitated.

Mikusch (*Z. anorg. Chem.*, 1908, **56**, 365) determined the solubility of zinc oxide in carbon dioxide solutions in equilibrium with basic zinc carbonate. By means of the above formula, it was found that the  $p_H$ 's of his solutions lay between 6.05 and 6.15. These hydron concentrations, though somewhat higher than that at which basic zinc carbonate began to separate in the present titration, viz.,  $p_H$  5.3, happen to be those that obtained during the main course of the precipitation. As zinc carbonate exists in equilibrium with

hydrogen ions at a relatively high concentration, it follows that water will decompose zinc carbonate to give the less soluble basic carbonate.

The hydrogen-ion concentration which had to be attained in the magnesium titration before sodium carbonate produced a precipitate shows that, contrary to the statements of several workers, the precipitate was basic. The solubility product of magnesium carbonate,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , at  $18^\circ$  is  $1.2 \times 10^{-4}$  (Johnson, *J. Amer. Chem. Soc.*, 1915, 37, 2014), and consequently, if complete dissociation be assumed, the solubility of magnesium carbonate is  $1.1 \times 10^{-2}$  mol. per litre. The solubility of magnesium hydroxide, obtained from the solubility product,  $2 \times 10^{-11}$ , is  $2.7 \times 10^{-4}$  mol. per litre. Hence, to precipitate the more soluble magnesium carbonate, a precipitant must be used which will supply the necessary carbonate ions without introducing the concentration of hydroxyl ions that causes the separation of magnesium hydroxide. As magnesium hydroxide is precipitated at  $p_{\text{H}}$  10.5, it is obvious that sodium bicarbonate ( $p_{\text{H}}$  8.7), even although added in large excess, cannot produce the corresponding concentration of hydrogen ions, and therefore cannot precipitate basic magnesium carbonate. It can, however, supply the carbonate ions which, provided that the magnesium salt solution is sufficiently concentrated, will cause magnesium carbonate to separate. Boussingault (*Ann. Chim. Phys.*, 1825, 29, 285) found that sodium sesquicarbonate,  $\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3$ , also could be used for this purpose. The data of Auerbach and Pick (*loc. cit.*) show that the  $p_{\text{H}}$  of such a mixture, decinormal with respect to carbonic acid, is approximately 9.9, which is just a little below the value required for the precipitation of the hydroxide.

No normal carbonates of chromium, beryllium, aluminium, thorium, and zirconium are known, and, as would be expected, the precipitates they form are highly basic. The shape of the beryllium titration curve appears to be peculiar to that element, and the precipitate did not appear until 22 c.c. (= 1.1 equivs.  $\text{Na}_2\text{CO}_3$  to 1 mol.  $\text{BeSO}_4$ ) of sodium carbonate had been added. In the chromium and thorium titrations, precipitation did not begin until 20 c.c. (1.85 equivs. to 1 Cr) and 18 c.c. (1.8 equivs.), respectively, of sodium carbonate had been added. As may be seen from Table III, the precipitation which took place from thorium chloride solution with sodium carbonate was due to the attainment of the  $p_{\text{H}}$  at which the hydroxide is precipitated and therefore the precipitate was basic. Chauvenet (*Compt. rend.*, 1911, 153, 66), having found that the analysis of such a precipitate corresponded to the formula  $\text{ThO}_2 \cdot \text{CO}_2 \cdot 8\text{H}_2\text{O}$ , stated that it was

normal thorium orthocarbonate,  $\text{ThCO}_4 \cdot 8\text{H}_2\text{O}$ , a salt of a purely hypothetical acid. In the case of the zirconium titration the curious effect noted in the borate titration was again observed, opalescence not beginning until 3.4 equivalents of sodium carbonate had been added and the relatively high  $p_{\text{H}}$  of 3.95 had been attained. In the borate titration the  $p_{\text{H}}$  was 4.06, and 3.4 equivalents of borax were required. As mentioned above, this phenomenon is believed to be due to suppression of the growth of the basic particles owing to a slight solvent action of the liberated weak acid.

### *Summary.*

(1) The hydrogen-ion concentrations which govern the precipitation of basic salts containing weak acid radicals—chromates, borates, and carbonates—have been investigated.

(2) These basic precipitates are formed at the same  $p_{\text{H}}$  as the respective hydroxides; cases occurred of delayed precipitation from zirconium and thorium chloride solutions.

(3) The precipitability of the different bases as basic salts depends on the capacity of the precipitant to produce the  $p_{\text{H}}$  at which the hydroxide is precipitated. In cases where this  $p_{\text{H}}$  is only just attained, the precipitation is partial.

(4) The conditions for the precipitation of normal salts have been discussed wherever possible.

(5) The mode of dissociation of chromic acid (J., 1924, 125, 1572) has been shown to account for the action of alkali-metal chromates in precipitating basic salts.

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## XXIII.—*Chloro-derivatives of m-Hydroxybenzaldehyde.*

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THE literature of this subject describes only 6-chloro- (no m. p. recorded) and 4 : 6-dichloro-3-hydroxybenzaldehydes (Friedländer and Schenck, *Ber.*, 1914, 47, 3044), 2 : 4 : 6-trichloro-3-hydroxybenzaldehyde (Krause, *Ber.*, 1899, 32, 123), and the conversion of

*m*-hydroxybenzaldehyde into aldehydotrichloroquino-dichloride by the action of chlorine in dilute acetic acid solution (Biltz and Kammann, *Ber.*, 1901, **34**, 4118).

The chlorination and the bromination (J., 1925, **127**, 876) of *m*-hydroxybenzaldehyde proceed in general on similar lines. A noteworthy difference is the production of 2-chloro-3-hydroxybenzaldehyde and but little of the 6-chloro-isomeride by direct monochlorination, bromination under similar conditions yielding 6-bromo-3-hydroxybenzaldehyde. The proportion of the 6-chloro-isomeride increases at high temperatures. The presence of water promotes trichlorination and renders regulated chlorination very difficult.

4-Chloro-3-hydroxybenzaldehyde was obtained in good yield from the corresponding 4-nitro-compound, but, as in the case of 6-bromo-3-hydroxybenzaldehyde (*loc. cit.*, p. 878), only poor yields of 6-chloro-3-hydroxybenzaldehyde were produced by a like procedure. This compound, however, was obtained in excellent yield by converting 2-chlorobenzaldehyde quantitatively into 2-chloro-5-nitrobenzaldehyde, reducing the oxime of this, diazotising the resulting 2-chloro-5-aminobenzaldoxime, and decomposing the product.

2 : 6- and 2 : 4-Dichloro-3-hydroxybenzaldehydes were obtained by direct chlorination of 2- and 4-chloro-3-hydroxybenzaldehydes, respectively, in glacial acetic acid solution, but 6-chloro-3-hydroxybenzaldehyde yielded a mixture of dichloro-compounds from which only the 2 : 6-isomeride could be isolated. In the direct dichlorination of *m*-hydroxybenzaldehyde the main product was the 2 : 6-dichloro-compound, Friedländer and Schenck's 4 : 6-dichloro-3-hydroxybenzaldehyde (*loc. cit.*) being isolated only in small quantity. The formation of the 2 : 6-dichloro-compound from both 2- and 6-chloro-3-hydroxybenzaldehyde proves the constitution assigned to it. The presence of the 4 : 6-dichloro-compound in the product of direct dichlorination of *m*-hydroxybenzaldehyde points to chlorination of the 6-monochloro-compound partially in the 4-position. Chlorination, however, takes place preferentially in position 2, and this preference is strong support for the constitution assigned to the 2 : 4-dichloro-compound obtained quantitatively from 4-chloro-3-hydroxybenzaldehyde.

The chloro-3-hydroxybenzaldehydes all have very pronounced sternutatory properties, which are most marked in the 2 : 6-, and but slightly less so in the 2 : 4 : 6-compound. For the monochloro-3-hydroxybenzaldehydes the order is 6-, 2-, and 4-. The property is comparatively feeble in the last compound, and thus is indicated its dependence on ortho-substitution. The property vanishes on methylation, but the methoxy-compounds have now acquired a hawthorn-like odour which in turn vanishes when these are oxidised

to the benzoic acids. All these compounds attack the moistened skin, producing painful blisters.

The colours produced by the action of alcoholic potash on the *p*-nitrophenylhydrazones are all claret and conform to Chattaway and Clemo's generalisation (J., 1923, 123, 3041).

The melting points of the ethers are considerably lower than those of the hydroxy-compounds, as in the case of the bromo-compounds (*loc. cit.*, pp. 878, 879), while those of their *p*-bromophenylhydrazones exhibit noteworthy diversity.

## EXPERIMENTAL.

### *Monochloro-3-hydroxybenzaldehydes.*

*2-Chloro-3-hydroxybenzaldehyde.*—(a) *Preparation by direct chlorination.* Through a solution of *m*-hydroxybenzaldehyde (50 g.) in glacial acetic acid (160 g.) at 15°, chlorine was bubbled (rate about 3 g. per hour) until the increase in weight was 29 g. After 12 hours, the colourless crystals of *2-chloro-3-hydroxybenzaldehyde* were filtered off (22 g.) and recrystallised from dilute acetic acid; m. p. 139·5° (Found: Cl, 22·5.  $C_7H_5O_2Cl$  requires Cl, 22·6%). The crystals become pale pink on prolonged exposure to air. On removal of 80 c.c. by distillation from the filtrate, a further crop (11 g.) was obtained, m. p. 138—140° after one recrystallisation. The solvent was then completely evaporated, and the dark residue (28 g.), m. p. 80—90°, resolved into two products by partial dissolution in hot aqueous sodium carbonate (10 g. of residue, 2 g. of  $Na_2CO_3$ , 50 c.c. of  $H_2O$ ) and extraction from the cold solution with ether. The compound thus removed (3—4 g.), after two crystallisations from dilute acetic acid, had m. p. 110° and was identified as 6-chloro-3-hydroxybenzaldehyde by comparison with the synthetic product from 6-nitro-3-hydroxybenzaldehyde (see later) and with the de-alkylated product from 6-chloro-3-methoxybenzaldehyde. On acidification of the sodium carbonate solution after ether extraction, *2-chloro-3-hydroxybenzaldehyde* was precipitated; this melted at 139·5° after crystallisation from dilute acetic acid.

The quantity of sodium carbonate to be used varies slightly with each chlorination experiment, the above being a good average and arrived at by trial, *viz.*, a sequence of additions, ether extractions, etc., until only 6-chloro-3-hydroxybenzaldehyde is extracted, this being much less acidic than the *2-chloro-isomeride*.

Catalysts such as ferric chloride, quinoline, quinoline sulphate, and iodine have no effect on the chlorination, which proceeds equally well in carbon disulphide, chloroform, or carbon tetrachloride, apart from difficulties arising through the volatility of the solvent. Chlorine in solution is less efficient than flowing chlorine.

The above process was repeated, a stream of bromine being substituted for the stream of chlorine. 6-Bromo-3-hydroxybenzaldehyde was produced as in the regulated bromination previously described (*loc. cit.*, p. 876), but in improved yield.

(b) *Preparation from 2-nitro-3-hydroxybenzaldehyde.* The nitro-compound was reduced with sodium hyposulphite (*loc. cit.*), the mixture just acidified at 0° (Congo-paper) with hydrochloric acid, and sodium nitrite and hydrochloric acid were then added alternately with stirring until diazotisation was complete. The diazo-solution was decomposed with cuprous chloride in the usual way, and the product distilled with steam. The large distillate was concentrated to small bulk after addition of sodium carbonate, and acidified. The product extracted therefrom with ether had m. p. 139.5° after recrystallisation from dilute acetic acid and also when mixed with 2-chloro-3-hydroxybenzaldehyde prepared by method (a) (Found : Cl, 22.55. Calc., Cl, 22.6%).

*Evidence for its constitution.* Two g. of the presumed 2-chloro-3-hydroxybenzaldehyde obtained in (a) were treated in aqueous 20% sodium hydroxide with methyl sulphate, and the methyl ether was removed in steam and crystallised from dilute alcohol. It melted at 57°, was identical with the methyl ether of the product obtained in (b), and depressed the m. p. (52°) of 4-chloro-3-methoxybenzaldehyde. On oxidation with alkaline permanganate (*loc. cit.*, p. 880), it yielded 2-chloro-3-methoxybenzoic acid, stout, colourless rectangles, m. p. 160° (Found : Cl, 18.8.  $C_8H_7O_3Cl$  requires Cl, 19.0%). 4-Chloro-3-methoxybenzoic acid forms needles, m. p. 215–216° (Found : Cl, 18.9%).

The *acetyl* derivative, m. p. 62° (Found : Cl, 18.0.  $C_9H_7O_3Cl$  requires Cl, 17.9%), and the *benzoyl* derivative, m. p. 88° (Found : Cl, 13.5.  $C_{14}H_9O_3Cl$  requires Cl, 13.6%), both separate from alcohol in stout, rhombic crystals. The *oxime* forms colourless needles, m. p. 149°, from diluted alcohol (Found : Cl, 20.8.  $C_7H_6O_2NCl$  requires Cl, 20.7%).

The *p-nitrophenylhydrazone* crystallises in orange-red, micro-crystalline needles, m. p. 244–245°, from hot alcohol (Found : N, 14.7; Cl, 12.0.  $C_{13}H_{10}O_3N_3Cl$  requires N, 14.4; Cl, 12.2%).

The *semicarbazone* forms pale yellow needles, m. p. 236–237° (Found : Cl, 16.5.  $C_8H_8O_2N_3Cl$  requires Cl, 16.6%).

*4-Chloro-3-hydroxybenzaldehyde.*—This compound was prepared from 4-nitro-3-hydroxybenzaldehyde by method (b) above and obtained in colourless needles, m. p. 121° (Found : Cl, 22.55.  $C_7H_5O_2Cl$  requires Cl, 22.6%).

The *oxime* separates from dilute alcohol in colourless needles containing water of crystallisation. These decompose at 106–110°.

The anhydrous needles melt at 126° (Found : Cl, 20.6.  $C_7H_5O_2NCl$  requires Cl, 20.7%). The *p*-nitrophenylhydrazone separates from dilute alcohol in violet-red needles, m. p. 226–227° (Found : Cl, 11.9.  $C_{13}H_{10}O_3N_3Cl$  requires Cl, 12.2%), and the semicarbazone crystallises in pale yellow needles, m. p. 238–239° (Found : N, 20.0.  $C_8H_8O_2N_3Cl$  requires N, 19.7%).

6-Chloro-3-hydroxybenzaldehyde.—(a) *Preparation from 6-nitro-3-hydroxybenzaldehyde*. This was carried out by process (b) above. The yield was very poor. The compound crystallised from dilute acetic acid in colourless needles, m. p. 111° (Found : Cl, 22.4.  $C_7H_5O_2Cl$  requires Cl, 22.6%).

(b) *Preparation from 2-chlorobenzaldehyde. Nitration*. The chloroaldehyde (16.5 g.) was added at 0–5° during 1 hour to a solution of sodium nitrate (11 g.) in 98% sulphuric acid (200 g.). After 30 minutes, the mixture was poured on to ice, and the solid product filtered off, washed with warm dilute sodium carbonate (yield 21 g.), and recrystallised from dilute acetic acid; m. p. 78–79° (Erdmann, *Annalen*, 1893, 272, 153, gives m. p. 80°). (On oxidation with alkaline permanganate it gives 2-chloro-5-nitrobenzoic acid, m. p. 165°.) *Reduction*. This proceeds normally with sodium hyposulphite, but the resulting 2-chloro-5-aminobenzaldehyde gave only a trace of 6-chloro-3-hydroxybenzaldehyde on decomposition by the usual diazotisation-steam distillation process. The chloronitrobenzaldehyde was therefore converted into its oxime, m. p. 143°, and a solution of this (5.5 g.) in 20 c.c. of aqueous sodium hydroxide (20%) and 100 c.c. of water was added gradually to a mixture of crystallised ferrous sulphate (50 g.), 20% sodium hydroxide (70 c.c.), and water (200 c.c.). After being stirred for 1 hour, the mixture was warmed to 30–40°, filtered, and the filtrate just acidified; 2-chloro-5-aminobenzaldoxime was then precipitated. This crystallised from alcohol in colourless plates, m. p. 159–160°, which turned brown in the air (Found : Cl, 20.7.  $C_7H_7ON_2Cl$  requires Cl, 20.8%). *Diazotisation and decomposition*. The aldoxime was redissolved by the addition of concentrated hydrochloric acid (20 c.c.), diazotised at 0° (sodium nitrite, 1.75 g.), and the solution decomposed by pouring it into boiling dilute sulphuric acid (20%). The 6-chloro-3-hydroxybenzaldehyde thus formed could be removed (very slowly) in steam, but was best extracted with ether. Yield, 3 g.

The oxime separates from dilute alcohol in colourless needles containing  $1H_2O$  (Found :  $H_2O$ , 10.0.  $C_7H_6O_2NCl \cdot H_2O$  requires  $H_2O$ , 9.5%), and from absolute alcohol in anhydrous needles, m. p. 146–147° (Found : Cl, 20.6.  $C_7H_6O_2NCl$  requires Cl, 20.7%). The *p*-nitrophenylhydrazone crystallises from dilute alcohol in red

needles, m. p. 250—251° (Found : Cl, 12.0.  $C_{13}H_{10}O_3N_3Cl$  requires Cl, 12.2%).

The semicarbazone forms pale yellow needles, m. p. 236° (Found : N, 19.9.  $C_8H_8O_2N_3Cl$  requires N, 19.7%).

*Dichloro-3-hydroxybenzaldehydes.*

2 : 6-Dichloro-3-hydroxybenzaldehyde.—(a) *Preparation by chlorination of 2-chloro-3-hydroxybenzaldehyde.* A solution of 5 g. of the aldehyde in glacial acetic acid (50 c.c.) was treated at room temperature (15°) with chlorine until the weight had increased by 2.5 g. (50 minutes). The white solid that separated crystallised from water in colourless needles, m. p. 140°. These melted at 116° when mixed with 2-chloro-3-hydroxybenzaldehyde (m. p. 139.5°) (Found : Cl, 36.8.  $C_7H_4O_2Cl_2$  requires Cl, 37.1%). On concentrating the solution to 20 c.c. the bulk of the product separated. It melted at 115—118°, and at 140° after two crystallisations from water (yield 6 g.). There were no coloured by-products such as were formed during monochlorination.

(b) *Preparation from m-hydroxybenzaldehyde.* Through a solution of 20 g. of the aldehyde in glacial acetic acid (90 c.c.), chlorine was passed until the increase in weight was 22 g. After an interval the rate of absorption slackened, presumably when monochlorination had taken place. The product (15 g.) was collected after 12 hours and fractionally crystallised from water. The more sparingly soluble 2 : 6-dichloro-3-hydroxybenzaldehyde separated in stout, white, rhombic crystals (yield 12 g.), m. p. 140°, identical with those obtained in (a) (Found : Cl, 36.9%). From the concentrated mother-liquor 1.5 g. of a homogeneous substance separated in needles, m. p. 129°. This was identified with the 4 : 6-dichloro-3-hydroxybenzaldehyde of Friedländer and Schenck (*loc. cit.*) and was evidently formed from the 6-chloro-3-hydroxybenzaldehyde produced in the initial monochlorination (see above).

(c) *Preparation from 6-chloro-3-hydroxybenzaldehyde.* A solution of 2 g. of the aldehyde in glacial acetic acid (15 g.) was chlorinated for 18 minutes. Crystals (0.5 g.) of 2 : 6-dichloro-3-hydroxybenzaldehyde separated (m. p. 140°; mixed m. p. 140°). On evaporating the filtrate, a mixture of dichloro-compounds (1.5 g.), m. p. 120°, was obtained which has defied resolution (Found : Cl, 36.8. Calc., Cl, 37.1%). It is probably a mixture of the 2 : 6- and 4 : 6-isomerides. The *p*-nitrophenylhydrazone prepared from it melts at a lower temperature than that of either of these two compounds.

The oxime of 2 : 6-dichloro-3-hydroxybenzaldehyde crystallises from dilute alcohol in clusters of felted needles, m. p. 174—175° (Found : Cl, 34.2.  $C_7H_5O_2NCl_2$  requires Cl, 34.5%) and the



*p*-nitrophenylhydrazone in deep orange-red needles, m. p. 205—206° (Found : Cl, 21.6.  $C_{13}H_9O_3N_3Cl_2$  requires Cl, 21.8%).

2 : 4-Dichloro-3-hydroxybenzaldehyde.—The crystals obtained quantitatively by the direct chlorination of 4-chloro-3-hydroxybenzaldehyde as in (c) above melted at 136—140°, and at 141° after crystallisation from dilute acetic acid. Mixed with 2 : 6-dichloro-3-hydroxybenzaldehyde (m. p. 140°), they melted at 111° (Found : Cl, 36.9.  $C_7H_4O_2Cl_2$  requires Cl, 37.1%).

The *oxime* crystallises from dilute alcohol in fine needles, m. p. 188° (Found : Cl, 34.3.  $C_7H_5O_2NCl_2$  requires Cl, 34.5%), and the *p*-nitrophenylhydrazone in orange-red needles, m. p. 277—278° (decomp.) (Found : N, 13.2; Cl, 21.6.  $C_{13}H_9O_3N_3Cl_2$  requires N, 12.9; Cl, 21.8%).

#### 2 : 4 : 6-Trichloro-3-hydroxybenzaldehyde.

This is obtained normally by trichlorination in glacial acetic acid solution. The crystals separate with acetic acid of crystallisation and immediately effloresce when exposed to air. They melt at 114°, and at the same temperature after they have been crystallised from dilute acetic acid (Krause, *loc. cit.*, gives m. p. 116°).

The *sodium* salt crystallises in pure yellow needles, which are sparingly soluble in water. The *oxime* separates from dilute alcohol in needles, m. p. 174° (Krause, *loc. cit.*, gives m. p. 170°) (Found : Cl, 44.1. Calc., Cl, 44.3%).

The *p*-nitrophenylhydrazone was prepared by mixing alcoholic solutions of the components at 70° and then adding one drop of water to the cooled mixture. Crystallisation was spontaneous and the product was then almost insoluble in alcohol. It crystallises in yellow-orange, microcrystalline needles, m. p. 272—273° (decomp.) (Found : Cl, 28.9.  $C_{13}H_8O_3N_3Cl_3$  requires Cl, 29.5%).

#### Methyl Ethers of the Chloro-3-hydroxybenzaldehydes.

These were prepared from the corresponding chloro-3-hydroxy- or nitro-3-methoxy-benzaldehydes by the methods used in the case of the bromo-compounds (Hodgson and Beard, *loc. cit.*, p. 878).

The following details of the methylation are reported because their adoption greatly improves the yield : a solution of 6-nitro- or 4-nitro-3-hydroxybenzaldehyde (20 g.) in water (100 c.c.) containing sodium bicarbonate (25 g.) is boiled and methyl sulphate (25 c.c.) gradually added with vigorous shaking. The mixture is heated under reflux for 15 minutes (not longer, else the yield is diminished), and the product filtered off on cooling (yield 18.5 g.).

6-Nitro-3-methoxybenzoic acid, prepared by alkaline oxidation of the aldehyde, has m. p. 255° (Rieche, *Ber.*, 1889, 22, 2347, gives

m. p. 132—133°). It crystallises in thick, colourless prisms (Found : N, 7.0. Calc., N, 7.1%). The silver salt is a white, crystalline solid (Found : Ag, 35.2. Calc., Ag, 35.5%).

*Nitration of 3-Methoxybenzaldehyde.*—Friedländer's method (*loc. cit.*) of adding the nitric acid "*auf einmal*" proved impracticable owing to the explosive violence of the reaction.

3-Methoxybenzaldehyde (20 g.) was added drop by drop during 2 hours to a mixture of 88.1% nitric acid (94 c.c.) and water (6 c.c.) maintained below 5°. The crude product (26.5 g.) obtained on pouring the mixture on to ice was washed, dried, and dissolved in hot benzene (80 c.c.). On cooling, 2-nitro-3-methoxybenzaldehyde (12 g.) separated in crystals, m. p. 98°, and more (3 g.) was obtained on concentrating the mother-liquor. Recrystallised several times from acetic acid, it melted at 102°. The material remaining in the benzene solution, consisting mainly of 6-nitro- mixed with a little 2-nitro-3-methoxybenzaldehyde, was distilled with steam and the 6-nitro-isomeride, which is the more volatile, was thus isolated. No 4-nitro-3-methoxybenzaldehyde was detected in the mixture, for on oxidation with alkaline permanganate this yielded an acid of m. p. 250° (6-nitro-, 2-nitro-, and 4-nitro-3-methoxybenzoic acids have m. p. 255°, 251°, and 208°, respectively).

*Properties of the Chloro-3-methoxybenzaldehydes.*—These all crystallise in colourless needles from dilute alcohol, sublime readily, and are very volatile in steam.

2-Chloro-3-methoxybenzaldehyde has m. p. 56° (Found : Cl, 21.0.  $C_8H_7O_2Cl$  requires Cl, 20.8%).

The oxime crystallises from dilute alcohol in stout needles, m. p. 130.5° (Found : Cl, 18.9.  $C_8H_8O_2NCl$  requires Cl, 19.1%), the *p*-nitrophenylhydrazone from alcohol in old-gold needles, m. p. 226—227° (Found : N, 14.0; Cl, 11.9.  $C_{14}H_{12}O_3N_3Cl$  requires N, 13.7; Cl, 11.6%), and the *p*-bromophenylhydrazone from alcohol in pale yellow plates, m. p. 155—156° (Found : N, 8.3.  $C_{14}H_{12}ON_2ClBr$  requires N, 8.2%. 0.1624 G. gave 0.1592 g. of mixed silver halides. Calc., 0.1585 g.).

4-Chloro-3-methoxybenzaldehyde has m. p. 52° and acquires a beautiful silver-grey colour on keeping (Found : Cl, 20.8%).

The oxime crystallises in colourless feathery needles, m. p. 98—99° (Found : Cl, 18.9%), the *p*-nitrophenylhydrazone in old-gold needles, m. p. 251° (Found : N, 14.1%), and the *p*-bromophenylhydrazone in pale pink, feathery crystals, m. p. 134° (Found : N, 8.0%).

6-Chloro-3-methoxybenzaldehyde has m. p. 62° (Found : Cl, 21.2%) and on oxidation (*loc. cit.*, p. 880) yields 6-chloro-3-methoxybenzoic acid, which crystallises in needles, m. p. 170—171°, from dilute acetic acid (Found : Cl, 18.8. Calc., Cl, 19.0%). Peratoner

and Condorell (*Gazzetta*, 1898, **28**, i, 197) give 171° as the m. p. of the acid prepared from 6-chloro-3-methoxytoluene.

The *oxime* forms fine needles, m. p. 101·5° (Found : Cl, 19·0%), the *p*-nitrophenylhydrazone crystallises in old-gold needles, m. p. 229° (Found : N, 14·0%), and the *p*-bromophenylhydrazone in pale yellow plates, m. p. 100° (Found : N, 8·0%).

2 : 6-Dichloro-3-methoxybenzaldehyde has m. p. 102° (Found : Cl, 34·9.  $C_8H_6O_2Cl$  requires Cl, 34·6%) and on oxidation yields 2 : 6-dichloro-3-methoxybenzoic acid, which crystallises in stout needles, m. p. 149·5°, from dilute alcohol (Found : Cl, 32·0.  $C_8H_6O_3Cl_2$  requires Cl, 32·1%).

The *p*-nitrophenylhydrazone forms old-gold needles, m. p. 214—215° (Found : Cl, 20·7.  $C_{14}H_{11}O_3N_3Cl_2$  requires Cl, 20·9%).

2 : 4-Dichloro-3-methoxybenzaldehyde has m. p. 82° (Found : Cl, 35·0%) and on oxidation yields 2 : 4-dichloro-3-methoxybenzoic acid, which crystallises in colourless needles, m. p. 163° (Found : Cl, 32·0%).

The *p*-nitrophenylhydrazone forms old-gold needles, m. p. 258—260° (Found : Cl, 20·7%).

2 : 4 : 6-Trichloro-3-methoxybenzaldehyde was prepared by methylating the hydroxy-compound. It is only slowly volatile in steam and crystallises from alcohol in stout needles, m. p. 76° (Found : Cl, 44·1.  $C_8H_5O_2Cl_3$  requires Cl, 44·4%). By very slow oxidation with alkaline permanganate it is converted into 2 : 4 : 6-trichloro-3-methoxybenzoic acid, which crystallises in needles, m. p. 109° (Found : Cl, 41·6. Calc., Cl, 41·7%). Zincke (*Annalen*, 1891, **261**, 239) gives m. p. 90°.

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD.

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## XXIV.—The Nitration of *m*-Bromophenol.

By HERBERT HENRY HODGSON and FRANCIS HARRY MOORE.

THE systematic study of the direct nitration of *m*-bromophenol does not appear to have been undertaken, although the following derivatives have been obtained by indirect means : 3-bromo-6-nitrophenol (Laubenheimer, *Ber.*, 1876, **9**, 1155), 3-bromo-6- and -4-nitrophenols (Auwers and Deines, *Zentr.*, 1924, **II**, No. 18), and 3-bromo-4 : 6-dinitrophenol (Körner, *J.*, 1876, **1**, 2317), Tijmstra (*Rec. trav. chim.*, 1902, **21**, 292) has described 3-bromo-2 : 4 : 6-trinitrophenol.

The present investigation on the direct nitration of *m*-bromophenol was carried out on similar lines to that of *m*-chlorophenol (J., 1925, 127, 1599). 2-, 4-, and 6-Nitro-3-bromophenols, 4:6-, 2:6-, and 2:4-dinitro-3-bromophenols, and 2:4:6- and 2:5:6-trinitro-3-bromophenols have been prepared in excellent yield. Their properties are very similar to those of the corresponding chloro-compounds.

3-Bromo-2-nitrophenol forms a remarkably labile, colourless hydrate, m. p. 35°, which changes on keeping, particularly in dry air, to a bright yellow, anhydrous form of m. p. 65—67°; this reverts to the colourless hydrate in moist air. The sensitiveness of the compound is such as to make it an approximate indicator of atmospheric humidity. This behaviour of the substance led to a further examination of the previously reported, colourless 3-chloro-2-nitrophenol (*loc. cit.*, p. 1601), which was found to be likewise a hydrate, but much more stable in air than that of the bromo-compound. Our analyst reported on a sample which he had thoroughly dried, but made no comment on the change of colour. This we ascribed at that time to atmospheric ammonia.) The analytical datum, therefore, is for anhydrous 3-chloro-2-nitrophenol.

Since 3-bromo-5-nitrophenol has been described by Blanksma (*Rec. trav. chim.*, 1892, 21, 254) and Heller and Kammann (*Ber.*, 1909, 42, 2191), the anhydrous substance mentioned above must have the only remaining constitution, *viz.*, that of 3-bromo-2-nitrophenol.

The order of increasing solubility in water of the three dinitro-compounds is: 2:6-, 4:6-, and 2:4-. They form characteristic silver salts, that of 3-bromo-4:6-dinitrophenol existing in three forms (two yellow and one red); Körner's observation (*loc. cit.*) is thus confirmed and supplemented.

The orientations tentatively proposed for the dinitro-compounds follow from the modes of preparation and by analogy with the corresponding chloro-compounds (*loc. cit.*). In addition is the following evidence: (1) All three dinitro-compounds are convertible into 3-bromo-2:4:6-trinitrophenol; the two nitro-groups in each compound are therefore in the meta-position with respect to each other. (2) The constitution of 3-bromo-4:6-dinitrophenol is definitely settled by its preparation from 3-bromo-4- and -6-nitrophenols and from 1:3-dibromo-4:6-dinitrobenzene. (3) 3-Bromo-2:6- and -2:4-dinitrophenols not only differ in melting point and solubility and in the properties of their silver salts, but the former can be prepared from both 3-bromo-2- and -6-nitrophenols, whereas the 2:4-dinitro-compound is obtainable

only from a sulphonated 3-bromo-2-nitrophenol. (4) The 2:6- and 2:4-dinitro-compounds both yield 2:4-dinitro-*m*-phenylenediamine when heated in a sealed tube with ammonia, and each specimen of this compound gives 2:4-dinitroresorcinol when boiled with aqueous sodium hydroxide. The vicinal positions of the four atoms or groups in each of these two bromodinitrophenols are thus established. Also these two compounds are converted into 2:4-dinitroresorcinol by boiling alkalis.

After prolonged sulphonation followed by treatment with excess of nitric acid, *m*-bromophenol gives a trinitro-sulphonic acid; this on hydrolysis yields 3-bromo-2:5:6-trinitrophenol, which is volatile in steam.

#### EXPERIMENTAL.

Unless otherwise stated, the methods of preparation of the 3-bromonitrophenols are those of the corresponding chloro-compounds (*loc. cit.*) with appropriate modifications.

##### *Mononitration of m-Bromophenol.*

(a) *By Sodium Nitrate and Sulphuric Acid* (*loc. cit.*, p. 1600).—3-Bromo-6-nitrophenol (yield 8.9 g. from 29 g. of *m*-bromophenol) is volatile in steam and crystallises from light petroleum in yellow prisms, m. p. 42°, having a characteristic odour (Auwers and Deines, m. p. 41.5–42.5°) (Found: Br, 36.7. Calc., Br, 36.7%). The methyl ether forms colourless plates, m. p. 85.5°, the benzoate crystallises in cream-coloured needles, m. p. 104°, and the sodium salt in scarlet needles. [The corresponding derivatives of 3-chloro-6-nitrophenol form colourless plates, m. p. 72°, colourless needles, m. p. 91°, and scarlet needles, respectively.]

3-Bromo-4-nitrophenol (yield 18 g.) is non-volatile in steam and crystallises from light petroleum in yellowish-white, odourless needles, m. p. 131° (Found: Br, 36.6. Calc., Br, 36.7%). It is also formed readily by oxidation of 4-nitroso-3-bromophenol (J., 1925, 127, 2262). The methyl ether crystallises in short, colourless needles, m. p. 45°, the benzoate in cream-coloured needles, m. p. 102°, and the sodium salt in amber needles. [3-Chloro-4-nitrophenol: methyl ether, short, colourless needles, m. p. 56.5°; benzoate, colourless needles, m. p. 96°; orange sodium salt.]

(b) *By Nitric Acid in Oleum* (*loc. cit.*, p. 1600).—On dilution of the nitration mixture and hydrolysis in a current of steam, the first distillates were oily, but from the later ones almost colourless needles separated on cooling; m. p. 35° (yield 13 g. or 60%). The product at first separated from light petroleum in bright yellow,

curly needles, m. p. 65—67°, but later crystals were admixed with the colourless product, which when separated mechanically had m. p. 33°. The yellow compound dissolves in aqueous sodium hydroxide to a red solution, from which the colourless variety is precipitated on acidification in the cold.

The yellow variety is anhydrous 3-bromo-2-nitrophenol (Found : Br, 36.6.  $C_6H_4O_3NBr$  requires Br, 36.7%). It has a characteristic odour distinct from that of 3-bromo-6-nitrophenol. The sodium salt crystallises in red needles, the methyl ether from dilute alcohol in white needles, m. p. 73° (Found : Br, 34.2.  $C_7H_6O_3NBr$  requires Br, 34.4%), and the benzoate from alcohol in white, feathery needles, m. p. 133° (Found : Br, 24.7.  $C_{13}H_8O_4NBr$  requires Br, 24.8%).

The colourless variety could not be dried in sufficient quantity for analysis owing to its ready conversion into the anhydrous form and in consequence its degree of hydration has not been determined.

3-Chloro-2-nitrophenol.—The anhydrous yellow variety, after prolonged drying over concentrated sulphuric acid, melts at 45—47° (Found : Cl, 20.6.  $C_6H_4O_3NCl$  requires Cl, 20.5%).

The hydrated white variety, crystallised from light petroleum, had m. p. 37.5—38° (Found : Cl, 18.5.  $C_6H_4O_3NCl \cdot H_2O$  requires Cl, 18.5%). On desiccation over concentrated sulphuric acid, 1.2108 g. lost 0.1128 g. after 20 hours and 0.1136 g. after 24 hours. The calculated loss for 1 mol.  $H_2O$  is 0.1138 g. (*M*, cryoscopic in phenol, 99.  $C_6H_4O_3NCl$  requires *M*, 173.5; and  $C_6H_4O_3NCl \cdot H_2O$  requires *M*, 96 if the water is completely abstracted by phenol).

#### *Dinitration of m-Bromophenol.*

The mixed acid referred to below contained 98% sulphuric acid (15 vols.), 70% nitric acid (12 vols.), and water (9 vols.).

3-Bromo-4 : 6-dinitrophenol.—(a) *m*-Bromophenol (4.4 g.) was added gradually to a mixture of 90.5% nitric acid (5 c.c.) and glacial acetic acid (5 c.c.), and after 12 hours the red solution was warmed for 30 minutes on the water-bath, poured into water, and steam-distilled. A little 3-bromo-6-nitrophenol passed over, followed by the main product, which solidified in colourless crystals, m. p. 90° (yield 2 g.). Recrystallised from light petroleum, this melted at 92° (Found : N, 10.7; Br, 30.4. Calc. for  $C_6H_3O_5N_2Br$  : N, 10.6; Br, 30.4%).

(b) 3-Bromo-6- and -4-nitrophenols (2 g.) were each added gradually to the mixed acid (8 c.c.) cooled in running water, the mixture was kept 2 hours, heated at 80° for 15 minutes, diluted, and steam-distilled. The product extracted from the distillate by ether crystallised from water or light petroleum in white needles,

m. p. 92°, in both cases. The liquor in the steam flask deposited in each case, on cooling, 3-bromo-2 : 4 : 6-trinitrophenol.

(c) 1 : 3-Dibromo-4 : 6-dinitrobenzene (3 g.) was boiled for 6 hours with aqueous sodium carbonate (3 g. in 20 c.c. of water), and the solution filtered hot and made just acid. The precipitate was crystallised from water; m. p. 92°.

The identity of the products in (a), (b), and (c) was established by the melting points of their mixtures.

The *silver* salt formed as a voluminous, yellow, gelatinous precipitate when a neutral solution of the ammonium salt was treated with aqueous silver nitrate. It gradually changed to a red, crystalline variety on keeping (the transition being accelerated by rubbing with a glass rod) which was but sparingly soluble in aqueous ammonia and in the presence of which conversion into a yellow, crystalline form occurred (Found : Ag, 29.0. Calc., Ag, 29.2%).

3-Bromo-2 : 6-dinitrophenol.—(a) This was obtained from a mixture of 1 g. of 3-bromo-2-nitrophenol and 4 c.c. of mixed acid (*loc. cit.*, p. 1602). The steam-volatile product solidified as a feathery, crystalline mass, m. p. 124°, and crystallised from light petroleum in colourless needles, m. p. 131° (Found : Br, 30.6.  $C_6H_3O_5N_2Br$  requires Br, 30.4%). A non-volatile product was 3-bromo-2 : 4 : 6-trinitrophenol.

(b) 3-Bromo-6-nitrophenol (4 g.) was slowly added to 7 c.c. of oleum (27%  $SO_3$ ) with cooling. The deep red solution was kept for 3 hours at 10°, then nitrated with 0.8 c.c. of nitric acid (90.5%) in 4 c.c. of oleum (27%  $SO_3$ ), and, after 1 hour, the mixture was poured into water.

Much decomposition occurred on hydrolysis but a small quantity of 3-bromo-2 : 6-dinitrophenol was obtained, m. p. 131° (Found : Br, 30.3%).

By the same procedure 3-chloro-2 : 6-dinitrophenol was obtained from 3-chloro-6-nitrophenol.

The red, crystalline *silver* salt is fairly easily soluble in water and readily in ammonia (Found : Ag, 29.1%).

3-Bromo-2 : 4-dinitrophenol was prepared as was 3-chloro-2 : 4-dinitrophenol (*loc. cit.*, p. 1602). The steam distillate deposited 3-bromo-2 : 6-dinitrophenol (0.7 g.), which was identified by its red silver salt, m. p. 131°, and by analysis (Found : Br, 30.5%). The filtrate gave to ether 0.8 g. of a product, probably 3-bromo-2 : 4-dinitrophenol, which crystallised from water in fine, silky, cream-coloured needles, m. p. 175° (Found : Br, 30.6.  $C_6H_3O_5N_2Br$  requires Br, 30.4%).

The yellow, crystalline *silver* salt was insoluble in ammonia (Found : Ag, 29%).

Attempts to prepare 3-bromo-2 : 4-dinitrophenol from 3-bromo-4-nitrophenol were unsuccessful owing to its decomposition during the sulphonation-nitration process described under (b) above.

*Separation of a Mixture of 3-Bromo-2 : 6- and -2 : 4-dinitrophenols.*—The mixture was converted, by the method described under 3-bromo-4 : 6-dinitrophenol above, into silver salts, which were digested with cold aqueous ammonia. The red silver salt of 3-bromo-2 : 6-dinitrophenol dissolved completely, the yellow isomeride was insoluble. The pure phenols liberated by hydrochloric acid had m. p. 131° and 175°, respectively.

*Action of Ammonia on 3-Bromo-2 : 6- and -2 : 4-dinitrophenols.*—These (1.3 g.) were separately heated in a sealed tube with concentrated ammonia (5 c.c.) to 150° during 2 hours. On cooling, the products were obtained quantitatively as brownish-yellow needles (0.9 g.) in each case, m. p. 258°. Recrystallised from water or glacial acetic acid, they melted, separately or mixed, at 258°. The substance was sparingly soluble in water, alcohol, ether, or glacial acetic acid (Found : N, 28.1 and 28.5, respectively. Calc. for  $C_6H_6O_4N_4$  : N, 28.3%). Barr states (*Ber.*, 1888, **21**, 1545) that 2 : 4-dinitro-*m*-phenylenediamine melts at 250° with partial decomposition. 4 : 6-Dinitro-*m*-phenylenediamine melts at about 300° (Nietzki and Schedler, *Ber.*, 1897, **30**, 1667).

The 2 : 4-dinitroresorcinol obtained from each of these products by the action of boiling aqueous sodium hydroxide melted, alone or mixed with the other, at 146° (Beilstein gives m. p. 142°) (Found : N, 14.1 and 13.9, respectively. Calc. for  $C_6H_4O_6N_2$  : N, 14.0%). Each product gave a red, gelatinous silver salt.

Mixtures of 3-bromo-2 : 6- and -2 : 4-dinitrophenols gave 2 : 4-dinitro-*m*-phenylenediamine when heated with ammonia as above, and 2 : 4-dinitroresorcinol on subsequent boiling with aqueous sodium hydroxide. Barr's statement (*loc. cit.*) that conversion into 2 : 4-dinitroresorcinol does not occur is therefore disproved.

Finally 3-bromo-2 : 6- and -2 : 4-dinitrophenols when separately boiled with aqueous sodium hydroxide gave the same 2 : 4-dinitroresorcinol of m. p. 146° and mixed m. p. 146°.

#### *Trinitration of m-Bromophenol.*

3-Bromo-2 : 4 : 6-trinitrophenol, prepared as was the corresponding chloro-compound (*loc. cit.*, p. 1603), is non-volatile in steam and crystallises from water in characteristic clusters of colourless, leaf-like forms, m. p. 149° (Tijmstra, *loc. cit.*, gives 144° for the m. p. of the compound crystallised from acetic acid) (Found : Br, 25.8. Calc., Br, 26.0%).

The same compound was also obtained by nitrating 3-bromo-



4:6-, -2:6-, and -2:4-dinitrophenols: 0.5 g. of each was dissolved, by gentle warming, in 98% sulphuric acid (3 c.c.), and the cooled solution treated with 70% nitric acid (1 c.c.) in 98% sulphuric acid (2 c.c.). After 3 hours, the solution was warmed on the water-bath for a few minutes and poured into water. On passage of steam, no volatile product was detected, and the solution, on cooling, deposited crystals of m. p. 149°. The yellow silver salt was insoluble in ammonia.

3-Bromo-2:5:6-trinitrophenol was prepared as was the chloro-compound (*loc. cit.*, p. 1603). It is volatile in steam and crystallises from water in fern-like clusters, m. p. 146° (Found: Br, 26.0.  $C_6H_2O_7N_3Br$  requires Br, 26.0%). The yellow silver salt is soluble in water but insoluble in ammonia.

Potassium 3-bromo-2:5:6-trinitrophenol-4-sulphonate, isolated during the above preparation, gave characteristic, yellow crystals from alcohol which exploded when heated [Found: S, 6.7; Br, 17.4. Calc. for  $C_6Br(OK)(NO_2)_3 \cdot SO_3K$ : S, 6.8; Br, 17.2%].

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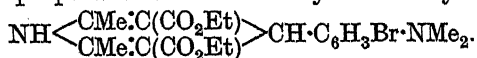
## XXV.—Condensation of 3-Bromo- and 3-Nitro-4-dimethylaminobenzaldehyde with Ethyl Acetoacetate and Ammonia.

By LEONARD ERIC HINKEL and WILLIAM REES MADEL.

ORTHO- and para-substituted aromatic dialkylamines do not react normally with nitrous acid (Würster and others, *Ber.*, 1879, **12**, 1796, 1816; Niementowski, *ibid.*, 1887, **20**, 1890; Koch, *ibid.*, p. 2459; Grimaux, *Compt. rend.*, 1891, **112**, 290, 727; Friedländer, *Monatsh.*, 1898, **19**, 627). We have observed that by the action of nitrous acid the aldehydo-group in *p*-dimethylaminobenzaldehyde is replaced by a nitroso-group, and that no action occurs with the corresponding 3-bromo- and 3-nitro-derivatives. It is to be expected, therefore, that the presence of a substituent in the ortho-position with respect to the dimethylamino-group will counteract any influence which this group may have on the reactivity of the aldehydo-group.

The behaviour of 3-bromo- and 3-nitro-4-dimethylaminobenzaldehyde in Hantzsch's pyridine synthesis has therefore been investigated, since it has been shown by one of us (J., 1920, **117**, 137)

that the introduction of a *p*-dimethylamino-group into benzaldehyde exerts a marked influence upon the condensation. In this case, not only is the yield of the dihydropyridine derivative considerably reduced, but the oxidation of the latter with nitrous fumes follows an unusual course, the dimethylaminophenyl group being eliminated as *p*-nitrosodimethylaniline. The dihydropyridine derivative readily yields a methiodide and a stable hydrochloride which is insoluble in water. In the condensation with 3-bromo-4-dimethylaminobenzaldehyde the effect of the introduction of the bromine atom is strikingly shown, not only in the greatly increased yield but also in the properties and the stability of the dihydrolutidine (I).



The oxidation of this compound proceeds quite normally with nitrous fumes. The dimethylamino-group, however, no longer reacts with methyl iodide even when heated under pressure, but the compound forms a hydrochloride which is very soluble in water. In this condensation the combined effects of the bromine and the dimethylamino-group cause the aldehyde to react in a manner closely resembling that of benzaldehyde.

With 3-nitro-4-dimethylaminobenzaldehyde the condensation proceeds normally. The yield of the product is not so great as in the preceding case, nevertheless it is considerably higher than that obtained from *p*-dimethylaminobenzaldehyde (*loc. cit.*), so that the influence of the nitro-group on the dimethylamino-group, although marked, is not so great as that of bromine. The stability of the dihydrolutidine derivative appears to be between those of the compounds derived from *p*-dimethylaminobenzaldehyde and its 3-bromo-derivative, since its oxidation with nitrous fumes must be more carefully regulated in order to prevent the elimination of the nitrodimehtylaminophenyl group. As in the previous condensation, the dihydrolutidine derivative does not form a methiodide, but is soluble in dilute mineral acids.

The further study of the effect of substituents in benzaldehyde upon the course of Hantzsch's pyridine synthesis is in progress.

#### EXPERIMENTAL.

*Ethyl 4-(m-Bromo-p-dimethylaminophenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate* (I).—3-Bromo-4-dimethylaminobenzaldehyde (1 mol.) dissolved in ethyl acetoacetate (2 mols.) was mixed with an alcoholic solution of ammonia (1 mol.). After remaining at the ordinary temperature for 1 hour, the mixture was heated for 7 hours in a closed flask. After removal of some of the alcohol the mixture solidified. The crude product crystallised from

alcohol in fine, yellowish-white needles (yield 82%), m. p. 133° (Found: Br, 17.5.  $C_{21}H_{27}O_4N_2Br$  requires Br, 17.7%). The ester is very soluble in dilute hydrochloric acid and is not hydrolysed even in the boiling solution.

*Ethyl 4-(m-Bromo-p-dimethylaminophenyl)-2:6-dimethylpyridine-3:5-dicarboxylate*.—Nitrous fumes were led into a thin paste of the dihydro-ester and alcohol until a clear solution was obtained. The viscous mass obtained after removal of the alcohol slowly solidified. It crystallised from aqueous alcohol in pale yellow crystals, m. p. 91° (Found: Br, 17.7.  $C_{21}H_{25}O_4N_2Br$  requires Br, 17.8%).

*Hydrolysis*. The ester (7 g.) was boiled for several hours with 30% alcoholic potassium hydroxide (50 c.c.). No potassium salt separated (compare J., 1920, 117, 140). The excess of potassium hydroxide was removed as carbonate, and the concentrated filtrate, after the addition of a small quantity of ether, deposited white crystals of the potassium salt.

*Ethyl 4-(m-Nitro-p-dimethylaminophenyl)-2:6-dimethyl-1:4-dihydropyridine-3:5-dicarboxylate*.—3-Nitro-4-dimethylaminobenzaldehyde (1 mol.), ethyl acetoacetate (2 mols.), and ammonia (1 mol. in alcohol) were heated together under the conditions previously described. After cooling, the solution was filtered from the crystals which had separated, and concentrated, a further crop being thus obtained. The product could be obtained in better yield by replacing ethyl acetoacetate and ammonia by ethyl  $\beta$ -aminocrotonate in alcoholic solution (yield 70%). The crude product crystallised from aqueous alcohol in deep yellow plates, m. p. 127° (Found: N, 10.3.  $C_{21}H_{27}O_6N_3$  requires N, 10.1%).

*Ethyl 4-(m-Nitro-p-dimethylaminophenyl)-2:6-dimethylpyridine-3:5-dicarboxylate*.—The oxidation of the dihydro-ester was carried out as previously described; the nitrous fumes were, however, led in very slowly and rise in temperature prevented by external cooling with water. As soon as the dihydro-ester had dissolved, the passage of nitrous fumes was discontinued; the solution almost immediately deposited crystals, and a further crop was obtained by concentrating the mother-liquor. The base crystallised from alcohol in large, yellow crystals, m. p. 109° (Found: C, 60.6; H, 6.1; N, 10.6.  $C_{21}H_{25}O_6N_3$  requires C, 60.7; H, 6.0; N, 10.1%).

We are indebted to Messrs. J. R. Geigy & Co. for a gift of the p-dimethylaminobenzaldehyde used in this investigation.

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XXVI.—*The Oxidation of Certain Sesquiterpenes with Chromyl Chloride and Chromic Acid.*

By DAVID TEMPLETON GIBSON, JOHN MONTEATH ROBERTSON, and JAMES SWORD.

THE action of chromyl chloride on the simple terpenes, as is the case with aromatic hydrocarbons, results in the formation of compounds of the formula  $C_{10}H_{16}, 2CrO_2Cl_2$ , which on treatment with water yield mixtures of oxidation products of the terpene and, as a rule, some chlorinated compounds (J., 1922, **121**, 2717; 1924, **125**, 107). Extending this work to the sesquiterpenes cadinene,  $\beta$ -caryophyllene, and cedrene, we now find that additive products are formed just as in the former instances, but there is a greater absorption of the reagent. The additive compound  $C_{15}H_{24}, 2CrO_2Cl_2$  apparently is contaminated with  $C_{15}H_{24}, 3CrO_2Cl_2$ , or perhaps with  $C_{15}H_{22}, 2CrO_2Cl$ . The amount of oxidising reagent required in its formation indicates the former. These compounds are not so sensitive to atmospheric moisture as those obtained from the simple terpenes and aromatic hydrocarbons; but when they are decomposed by water they yield only a relatively small amount of tractable oxidation product.

Étard (*Ann. Chim. Phys.*, 1881, **22**, 218) states that the chromyl chloride additive product of toluene is decomposed by ether, ethyl chloride being evolved. We find, however, that ether carefully dried over sodium has no action whatever either on the toluene additive compound or on the new series of compounds we have prepared.

$\beta$ -Caryophyllene forms an additive compound having the approximate composition  $C_{15}H_{24}, 2\frac{1}{2}CrO_2Cl_2$ . On decomposition with water, this yields a ketone,  $C_{15}H_{24}O$  (which gave a crystalline *semicarbazone*), an *unsaturated ketone*,  $C_{15}H_{20}O_2$ , caryophyllene alcohol, and some chlorinated oxidation products, but no aldehyde.

From cedrene, an additive compound of similar composition was obtained, which on decomposition yielded a compound,  $C_{15}H_{24}O$ , which gives a *semicarbazone*, together with chlorinated products. The compound  $C_{15}H_{24}O$  does not give an acid upon further oxidation with nitric acid, and is therefore probably not an aldehyde.

When the additive compound obtained from cadinene was decomposed, in addition to a small quantity of an acid, a 10% yield of a steam-volatile, *neutral product* was obtained which did not give a crystalline semicarbazone. Owing to the difficulty of preparing this hydrocarbon, we did not consider that the yields justified the continuation of this part of the investigation, and it seemed probable

that a direct oxidation with chromic acid might lead to more valuable results.

Wallach (*Annalen*, 1887, 238, 87) found that, on oxidation with chromic acid, cadinene gave a mixture of lower fatty acids. With potassium dichromate and sulphuric acid mixture, we obtained products which were entirely acid. On careful oxidation with chromic anhydride, however, we obtained a *compound*, b. p. 180—196°/12 mm., the composition of which agrees with the formula  $C_{15}H_{24}O_2$ . No definite evidence of the presence of ketonic or hydroxyl groups could be obtained. When treated with metallic sodium, the compound polymerised. This compound closely resembles the hydroxy-ketone described by Ruzicka and Stoll (*Helv. Chim. Acta*, 1924, 7, 94).

#### EXPERIMENTAL.

In each case described below, the additive compound was prepared by allowing the reagents to react in carbon tetrachloride solution at such dilution (10%) as allowed the course of the reaction to be carefully controlled.

*Action of Chromyl Chloride on  $\beta$ -Caryophyllene.*— $\beta$ -Caryophyllene, b. p. 119°/9 mm.,  $n_D^{20}$  1.5030,  $[\alpha]_D^{25}$  — 5.2°, gave an additive product which had the approximate composition  $C_{15}H_{24} \cdot 2\frac{1}{2}CrO_2Cl_2$  and remained unaltered when different proportions of chromyl chloride were used (Found: Cr, 21.0, 20.9, 21.3.  $C_{15}H_{24} \cdot 2CrO_2Cl_2$  requires Cr, 20.0%.  $C_{15}H_{24} \cdot 3CrO_2Cl_2$  requires Cr, 23.3%). It was decomposed in the usual way. The steam-distilled oil (17 g. from 75 c.c. of caryophyllene) was fractionated at 1 mm., and a main product (10 g.), b. p. 120—140°, Cl, 5%, was collected. This fraction was practically freed from chlorine by refluxing with zinc dust in alcoholic solution for a month. The oil thus purified distilled mainly at 100—110° (A) and 110—125° (B) at 0.5 mm. (A), which was saturated, was treated (5 g.) in the usual way with semicarbazide acetate, being allowed to stand 2 months. After removal of the solvent and uncombined oil, the residue was recrystallised from methyl alcohol, and the resulting semicarbazone (1 g.), after further purification from benzene, melted at 234° (Found: C, 69.3; H, 10.0; N, 15.4.  $C_{15}H_{24}ON_3$  requires C, 69.4; H, 9.8; N, 15.2%).

The uncombined oil on evaporation deposited crystals which, after washing with ligroin, melted at 92—95° and did not depress the melting point of an authentic specimen of caryophyllene alcohol.

The higher fraction (B) gave a non-crystalline semicarbazone which, after removal of solvent and uncombined oil, was distilled in steam with oxalic acid, and the regenerated oil collected. It was

unsaturated; b. p.  $118^{\circ}/1$  mm. (Found: C, 77.8; H, 9.4.  $C_{15}H_{20}O_2$  requires C, 77.6; H, 8.9%).

*Action of Chromyl Chloride on Cedrene.*—Cedrene, b. p.  $123-125^{\circ}/8$  mm.,  $d_4^{20}$  0.9361,  $[\alpha]_D^{17} - 55.4^{\circ}$ ,  $n_D^{17}$  1.50170, gave an additive compound similar to the one described above. When it was decomposed, steam-distillation of the product gave an oil which contained chlorine (Found: Cl, 4.2%). The chlorine content was reduced to 0.5% by refluxing in alcohol with zinc dust for 8 weeks. The oil then distilled at  $93^{\circ}/0.15$  mm., and the distillate contained no chlorine;  $n_D^{15}$  1.5462 (Found: C, 81.0; H, 10.6; *M*, cryoscopic in benzene, 224, in camphor, 223.  $C_{15}H_{24}O$  requires C, 81.7; H, 11.0%; *M*, 220).

The oil gave a good yield of an amorphous semicarbazone, which was dissolved in methyl alcohol to free it from the solid condensation product which semicarbazide forms with itself, purified with animal charcoal, and added to a large excess of water. This retained the last traces of the condensation product and precipitated the *semicarbazone* as a white powder (Found: C, 70.4; H, 10.0; N, 14.4.  $C_{15}H_{27}ON_3$  requires C, 69.4; H, 9.8; N, 15.2%).

*Action of Chromyl Chloride on Cadinene.*—Cadinene, b. p.  $130-134^{\circ}/10$  mm.,  $d_4^{20}$  0.9189,  $n_D^{20}$  1.5097,  $[\alpha]_{488}^{15} - 125^{\circ}$ , regenerated from the dihydrochloride, m. p.  $118^{\circ}$ , gave an additive compound of similar composition to those described above. On decomposition, it yielded a small quantity of a non-crystalline acid, and a neutral product in about 10% yield, consisting of a steam-volatile oil, which was mixed with semicarbazide acetate, but even after prolonged treatment no crystalline semicarbazone could be obtained.

*Chromic Acid Oxidation of Cadinene.*—Chromic anhydride (70 g.) dissolved in a little water and diluted with acetic acid was slowly added with constant stirring to cadinene (50 g.) in glacial acetic acid (250 g.) during 1 hour, the temperature being kept below  $50^{\circ}$  by occasional cooling. Finally the mixture was heated on the water-bath until green, and water added. The neutral product was isolated and purified by fractional distillation at 0.5 mm. After removal of unchanged cadinene (dihydrochloride, m. p.  $118^{\circ}$ ) and a small amount of acid, a light yellow oil was obtained, b. p.  $180-196^{\circ}/12$  mm.,  $n_D^{25}$  1.5095 (Found: C, 76.6; H, 10.2.  $C_{15}H_{24}O_2$  requires C, 76.3; H, 10.2%).

This oil was unsaturated towards bromine and alkaline permanganate. It did not give a semicarbazone, neither did it react with *p*-nitrobenzoyl chloride, or with phenylcarbimide. Addition of finely divided sodium produced polymerisation.

The acid products of the oxidation were isolated and purified.

The chief product gave the following analysis: C, 59.2; H, 8.4%. The silver salt gave Ag, 35.4%.

Cadinene (10 g.) in acetic acid (50 c.c.) was treated with potassium dichromate (20 g.) and sulphuric acid (14 c.c.) in aqueous acetic acid. The reaction was similar to that described above. After a little unchanged cadinene had been removed, there resulted only an acid product which appears to be identical with the acid described above (Found: C, 59.7; H, 8.6%. Silver salt gave Ag, 35.1%).

We desire to express our thanks to Professor G. G. Henderson for the interest which he took in this work, and to the Carnegie Trust for a grant which helped to defray the expense.

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## XXVII.—*Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part I. Selenium Dioxide.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and JOHN O'NEIL MILLOTT.

THE action of hydrofluoric acid on selenious compounds does not appear to have been studied, except perhaps with negative results, no doubt on account of the unstable and corrosive nature of the reagents and of such compounds as they might be expected to form. Hydrofluoric acid probably does not form a definite product as it does with tellurium dioxide. A solid oxyfluoride of selenium was prepared by Moissan ("Le Fluor," p. 123) by the action of fluorine on selenium, but was not analysed. In the present research anhydrous hydrogen fluoride was used.

A remark of Ditte (*Compt. rend.*, 1876, **83**, 225) bears on the present research, *viz.*, that hydrofluoric acid is energetically absorbed by selenium dioxide; the product, however, was not examined.

*Preparation of the Selenium Dioxide.*—The method used was substantially that of Divers and Haga (*J.*, 1899, **75**, 537). The selenium was dissolved in concentrated nitric acid and after several evaporations to dryness with water the product was transferred hot to a long glass tube and sublimed in a current of oxygen dried by calcium chloride and phosphoric oxide. The product was white or pink and we consider that it was dry; the test for dryness described by Prideaux and Green (*J. Physical Chem.*, 1924, **28**, 1274) was applied. The oxide, dissolved in dry alcohol, did not immediately redden litmus paper. Also a sample, heated with anhydrous copper sulphate, gave no blue colour.

*Preparation of Hydrogen Fluoride.*—Commercial sodium hydrogen

fluoride of high quality and practically dry was finely ground and strongly heated before each distillation. This was carried out in a copper apparatus. The still, still-head, and receiver were made by Mr. E. R. Walter, B.Sc.Eng., whose skill and advice have been much appreciated. The still-head was fitted with an additional tube through which a current of dry air could be blown. The straight condenser cooled by ice-water was succeeded by a spiral condenser cooled by ice and salt. After the first runnings the liquid hydrofluoric acid was colourless and immediately gelatinised filter-paper. The receiver was then screwed on. It contained a platinum crucible, in which the acid collected, and was cooled by ice or a freezing mixture. The vapour passing on was dry, as the condensed acid would retain any traces of water. It passed over the selenium dioxide, which was usually contained in a platinum bottle supplied with platinum inlet and outlet tubes. The vapour then passed through a bubble-counter containing dry chloroform, and finally through a soda-lime tube.

The hydrogen fluoride was rapidly absorbed by the selenium dioxide, which liquefied and became warm. The liquid first formed was not analysed, but it contained quite a small proportion of hydrogen fluoride, the selenium dioxide being very soluble. As the hydrogen fluoride bubbled into the liquid it was continually absorbed. The experiment was stopped usually when the liquid contained 40 to 50% of hydrogen fluoride. This does not represent the limit of absorption from the acid vapour at a pressure somewhat below one atmosphere. In one experiment, a boat gained weight until the hydrogen fluoride was 75% of the total weight.

*Properties of the Product.*—The liquids formed were colourless and mobile. They fumed strongly and at the ordinary temperature the fumes consisted of hydrogen fluoride only. No volatile selenium compound was trapped in the chloroform (or alcohol) bubble-counter. The liquid does not mix with chloroform, but forms a layer below it. It rapidly attacks copper, forming a dark substance. In absence of water it slowly attacks glass. When allowed to evaporate in a desiccator with reagents which absorb water and hydrogen fluoride, it slowly dries up to a syrup. If water is present, as it was in some of our earlier experiments, crystals of selenious acid are formed, retaining less than  $\frac{1}{2}$ % of hydrogen fluoride.

*Distillation.*—The product was distilled from the platinum bottle and condensed in a long platinum tube cooled with ice-water. Distillation began at about 65°, continued freely to about 85°, then fell off; little was obtained above 100° until much higher temperatures were reached. The distillate contained more selenium dioxide than can be accounted for by its vapour pressure, which



is 12.5 mm. at 70° and 40.6 mm. at 199° (Jannek and Meyer, *Z. anorg. Chem.*, 1913, **83**, 60). An analysis of the distillate is given in the first line of the table. The residue in the flask was analysed by the volumetric method. The distillate was treated with dry ether, which gave an immediate white precipitate. After washing with more ether, this contained 96 mol.% of selenium dioxide and 4 of hydrogen fluoride. In another experiment the residual liquid, from which much solid had been frozen, was distilled with sulphuric acid (the monohydrate). A yellow, fuming liquid came over at 120° to 130°. This reacted violently with water, giving a solution which contained both selenious and hydrofluoric acids, but no sulphuric acid.

The residue in the bottle after distillation (without sulphuric acid) contained slightly more than 5 mols. of hydrogen fluoride to 1 of selenium dioxide. This is the composition at which the vapour pressure of the hydrogen fluoride sinks to low values. At higher temperatures, the liquid would probably distil as a whole, with dissociation.

*Separation of Solid.*—Preliminary experiments showed that when the liquid was strongly cooled by alcohol-solid carbon dioxide, a white solid separated which had a composition similar to that of the liquid left after the distillation of the more volatile part. The cooling curves of this system were determined in various forms of apparatus. The arrests were variable and not well marked. This was probably due, partly to the nature of the liquid, which can be greatly supercooled, and partly to the difficulty of securing good heat transference and suitable thermal capacity in apparatus which contained so corrosive a liquid.

The freezing points were therefore determined by observation of the contents of the platinum bottle or crucible in which was placed the thermometer in a protecting tube. A portion of solution B, containing about 4.5 mols. of hydrogen fluoride to 1 of selenium dioxide, was poured into a crucible, which was cooled by direct immersion in alcohol-carbon dioxide at -70°. When crystallisation had once started, it proceeded very rapidly. The solid was allowed to melt slowly in a second crucible cooled externally. The temperature was constant at -17.5°, when about one-third was solid, and fell slowly to -18°, when about three-quarters was solid.

*Methods of Analysis.*—From what is known of the strengths of hydrofluoric and selenious acids it should be possible by a volumetric method to determine approximately the amounts of each in a mixture; the greater part of the hydrofluoric acid being titrated with the first hydron of the selenious acid with *p*-nitrophenol as indicator, and the second with an indicator of alkaline

end-point. According to the results of Wilcoox and Prideaux (J., 1925, 127, 1543) the end-point in a titration of 0.05 *N*-selenious acid is at  $p_H = 10.35$ ; the corresponding value from Blanc's second constant is 9.70 (*loc. cit.*). Our solutions were about normal, and from the equation  $2p_H = p_k + p_{kw} + \log c$ , putting  $\log c = 0$  and using our second constant  $k_2 = [H^+][\text{SeO}_3^{''}]/[\text{HSeO}_3'] = 0.87 \times 10^{-8}$ , the end-point will be at  $p_k = 11.0$ . The most suitable indicator available was thymolphthalein, the transition interval of which is 9.3 to 10.5. Titrations to a full blue should still be slightly below the correct end-point of the dibasic acid. This was confirmed with 10 c.c. of solutions of selenious acid.

1st end-point $\times 2$ .....	11.7	11.6	10.8
2nd end-point .....	11.6	11.5	10.65

Hydrofluoric acid is usually titrated with phenolphthalein on account of the lower degree of the second dissociation of  $\text{H}_2\text{F}_2$ . Titrations first with *p*-nitrophenol and then with phenolphthalein showed that most of the acid was neutralised at the change-point of the former indicator, the factor for converting the former into the latter titres being (on the average of several results) 1.03. The effect of the short titration with thymolphthalein on the total acid titre is negligible, and it is completely overcome by the more important error in the *p*-nitrophenol end-point of the mixed acids, which makes the volumetric estimation of selenious acid too high. The necessary corrections were determined by the following titrations of known mixtures.

	Acids separately.		Acids together.	
C.c. of alkali with <i>p</i> -nitrophenol	(a) 13.04	(b) 13.98	(a) 12.90	(b) 13.80
" " thymolphthalein	(a) 18.45	(b) 19.39	(a) 18.40	(b) 19.30

Thus the result of the *p*-nitrophenol titration must be multiplied by a factor, 1.01, to give the sum of the titrations of the acids separately, *i.e.*, of the hydrofluoric acid and the first hydrion of the selenious acid. This corrected titration subtracted from the total titration (with thymolphthalein) gives the amount of selenious acid. This difference, subtracted from the corrected titration with *p*-nitrophenol, gives the amount of hydrofluoric acid estimated by this indicator; and the latter, multiplied by 1.03, gives the amount of hydrofluoric acid estimated by phenolphthalein. The corrected ratios of hydrogen fluoride to selenious acid so obtained are lower than those determined gravimetrically. We have not been able to determine the reason of this discrepancy. It is possible that the hydrolysis is not quite complete, and that there is some complex formation even in aqueous solutions which diminishes the "strong acid" titration.

Selenium was determined gravimetrically by the usual method,

*i.e.*, by precipitation with sulphur dioxide from rather concentrated hydrochloric acid. In the later experiments the modification of Lenher and Kao (*J. Amer. Chem. Soc.*, 1925, 47, 772) was employed. The selenium was precipitated from dilute hydrochloric acid, filtered off as red selenium in the cold, washed successively with concentrated hydrochloric acid, water, alcohol, and ether, dried at 30—40°, then to constant weight at 120—130°. Under these conditions, no water or salts are included in the precipitate.

*Analysis.*—Attempts were made to determine the fluorine also as calcium fluoride in the presence of calcium selenite. These gave rather variable results which were low in fluorine compared with those of the two methods on which we placed most reliance. Some of the results are given in brackets under the gravimetric results in column 6 of the table, which are based on the weight of solid taken and the gravimetric selenium. Column 7 is obtained by subtracting the equivalents of selenium (gravimetric) from the total equivalents of the two acids given by the thymolphthalein titrations. The difference gives the weight of hydrogen fluoride. The sum of the selenium dioxide and the hydrogen fluoride should be equal to the weight of the solid taken. Results in which there was not a fair agreement have not been included.

Preparation A consisted of 19.43 g. of liquid which contained 69.3% HF. The molar ratio by increase of weight was 12.5:1. This was used to determine cooling curves. The first marked arrest on the cooling curve was at  $-54^{\circ}$ , the last on the heating curve, at  $-29^{\circ}$ . The liquid was then distilled up to  $+85^{\circ}$ . The analysis of the distillate is given in the table. The residue, by titration only, contained hydrogen fluoride and selenium dioxide in the ratio 4.9. Two samples of solid separated from the mother-liquor and titrated without weighing gave ratios of 4.9 and 4.93.

Preparation B weighed 21.91 g. and the molar ratio by increase of weight was 4.425. The initial arrest on the cooling curve was at  $-22.5^{\circ}$ . The solid  $B_1$  was frozen out and analysed. The residue in the bottle, which had now been reduced to 14.8 g., was poured into a crucible and the freezing point determined as described above. The remaining samples of B were then taken and analysed.

The filtration of  $B_1$  was done in the usual way, except that the crucible was surrounded by a glass tube, containing lumps of solid carbon dioxide and closed at the top by a stopper in which was a calcium chloride tube to dry the incoming air. The platinum Gooch crucible contained dried asbestos fibre, above which was a false bottom of platinum foil perforated with needle holes. The liquid which had run through the asbestos was rejected. The solid was removed quickly and weighed in a closed crucible. Sample

$B_2$  was pressed on the Gooch crucible with the false bottom but without the asbestos. It was kept cold inside another crucible in the freezing mixture. Sample  $B_3$  was washed with dry cold chloroform by decantation and dried with filter-paper until strong fuming began. Preparation  $C$ , 17.54 g., had a molar ratio of 4.62 to 1. The fractions  $C_1$  and  $C_2$  were obtained by partial freezing and decantation of the liquid part; the solid was then broken up, stirred, and dried with filter-paper.  $C_3$  was collected from the hard solid which first formed round the edge at the top.

The use of the analytical results in making the table is exemplified for sample  $C_1$ . 1.756 Grams of solid give 0.651 g. or 0.00822 gram-atom of selenium, which is equivalent to 0.915 gram of the dioxide. The difference in weight between the original substance and the dioxide, *i.e.*, 1.756—0.915, is taken as the quantity of hydrogen fluoride (gravimetric) and is 0.04205 mol. The molar ratio of hydrogen fluoride (gravimetric by difference) to selenium dioxide (gravimetric) is therefore  $0.04205/0.00822 = 5.1$ . 1.756 Grams of solid require 58.58 c.c. of 0.988 *N*-alkali, with thymolphthalein as indicator. By subtracting from the total milliequivalents of acid, *i.e.*, 57.66, the equivalents of selenious acid, *i.e.*, 0.01645, the equivalent of hydrogen fluoride is found to be 0.0412. The ratio hydrogen fluoride (volumetric by difference) to selenium dioxide (gravimetric) is 5.0.

The weight of hydrogen fluoride so found (volumetric by difference), *i.e.*, 0.824 g., when added to the selenium dioxide, 0.918 g., gives the weight of product calculated from the volumetric total acid and gravimetric selenium; *i.e.*, 1.739. These are the values in brackets in column 2.

Description of preparation and sample.	Wt. taken. Wt. calc. from analysis in brackets.	Ratio $n\text{HF}/\text{SeO}_2$ from gravimetric selenium and total wt. of sample.	Ratio $n\text{HF}/\text{SeO}_2$ from gravimetric selenium and total acid found.
Distillate at 85° and over (p. 168).	0.5435 (0.507)	14.65	12.85
$B_1$ . Solid sucked dry on cooled Gooch.	0.5405 (0.5124)	4.5	4.5
$B_2$ . Solid dried by pressing on Gooch.	3.56 (3.47)	4.93	4.94
$B_3$ . Solid washed with cold chloroform.	1.236 (1.170)	5.3	4.8
$C_1$ . Solid, first fraction dried with filter- paper.	1.756 (1.739)	5.15	5.0
$C_2$ . Solid, second fraction.	0.984 (0.998)	4.55	4.45
$C_3$ . Solid first formed on surface.	0.6695 (0.664)	—	(4.9) Corrected volumetric as on p. 170.
$C_4$ . Liquid, mother-liquor of $C_1$ and $C_2$ .	2.770 2.83	4.14	4.34

*Summary and Conclusions.*

The analyses show that the solid frozen out of our liquid product contains constantly about 5 mols. of hydrogen fluoride to 1 mol. of selenium dioxide. The fluctuations are, we consider, due to inclusion of mother-liquor, to the loss of variable quantities of hydrogen fluoride, and to other difficulties inherent in the analysis of so corrosive a substance. This additive compound,  $\text{SeO}_2 \cdot 5\text{HF}$ , is in equilibrium with liquids of various compositions. It dissociates in the vapour phase, giving off small quantities of hydrogen fluoride, the vapour pressure of which is only a small fraction of that of the pure acid. At higher vapour pressures the dissociation of the vapour which contains selenium dioxide is not complete. Thus the same compound is obtained either by distillation of the excess of hydrogen fluoride or by freezing from liquids of different compositions.

The above is one of the few examples of complex formation between hydrogen fluoride and an acid anhydride. Analogous compounds with tellurous anhydride have been prepared by Metzner (*Ann. Chim. Phys.*, 1898, 15). These were prepared from aqueous hydrogen fluoride. One of them was much hydrated;  $2\text{TeF}_4 \cdot 3\text{TeO}_2 \cdot 6\text{H}_2\text{O}$ . The other, given as  $\text{TeF}_4 \cdot \text{TeO}_2 \cdot 2\text{H}_2\text{O}$ , might of course be written as  $2\text{TeO}_2 \cdot 4\text{HF}$ . We have prepared a compound somewhat similar to this from anhydrous hydrogen fluoride which we hope to describe in a later communication. The probabilities of the two formulæ are evenly balanced in the case of tellurium, but in the case of selenium we consider the latter, or additive compound, formula far more probable. The fluoride of so strongly electronegative an element is probably not formed under conditions which involve elimination of water, or at any rate, if there is some anhydrous fluoride in the presence of a large excess of hydrogen fluoride, it would be very difficult to prove its presence and isolate it. Up to the present, no fluorides or oxyfluorides of quadrivalent selenium have been described, with the important exception of the compound, afterwards claimed to be the hexafluoride, described by Lebeau (*Compt. rend.*, 1906, 144, 1042). His first preparation, the analysis of which corresponded to  $\text{SeF}_4$ , had the properties to be expected and also resembled our present compound. It was a colourless liquid, boiling at about  $+100^\circ$ , and solidifying at  $-80^\circ$ . It decomposed water, giving hydrofluoric and selenious acids in the molar ratio 4 : 1.

A comparison between the actions of hydrogen fluoride and hydrogen chloride on selenium dioxide is instructive. Hydrogen chloride also gives in the first place an additive compound, which, however, easily loses water, giving the oxychloride  $\text{SeOCl}_2$  (Lenher, *J. Amer. Chem. Soc.*, 1920, 42, 2498). Loss of water from our

compound did not take place under the conditions tried and is unlikely in the case of the compound obtained from hydrogen fluoride on account of the order of the affinities of fluorine and oxygen for hydrogen.

The apparatus required in the preparation of the hydrogen fluoride, and the platinum used in the manipulation of the products were obtained by means of a grant from the Royal Society, which is gratefully acknowledged. The selenium was kindly presented by the Baltimore Copper Company.

The thanks of one of us (J. M.) are also due to the Department of Scientific and Industrial Research for a maintenance grant.

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## XXVIII.—*The Hydration of Strong Electrolytes, the Viscosity of their Aqueous Solutions, and the Dilution Law.*

By JAMES NETHERWOOD SUGDEN.

MANY attempts have been made to determine the hydration of strong electrolytes in aqueous solution. The results of different methods of investigation differ widely, some yielding relatively small hydration numbers, up to 20 molecules of water per molecule of a hydrated salt, whereas others give much larger values which are quoted in many text-books (e.g., Nernst's "Theoretical Chemistry," 1923, p. 450; Freundlich, "Kapillarchemie," 1923, p. 81). In consequence of this uncertainty, it has not hitherto been possible to apply a hydrate theory to those properties of salt solutions which may be expected to depend on the hydration of the solute. An attempt has been made in this paper to apply, in a quantitative way, a new hydrate theory which is put forward as a result of the experimental work outlined in subsequent sections.

### *Determination of Hydration Numbers.*

It has been shown by Frazer and Myrick (*J. Amer. Chem. Soc.*, 1916, **38**, 1907), Scatchard (*ibid.*, 1921, **43**, 2406), and Washburn (*Tech. Quart.*, 1908, **21**, 373), from the osmotic pressure, vapour pressure, and freezing-point depression respectively, that at moderate temperatures and at concentrations as high as molar, sucrose behaves as if it formed a hexahydrate in solution, and this fact forms a convenient starting point for testing other methods which are applicable both to electrolytes and to non-electrolytes. One such method was indicated by Philip (*Trans. Faraday Soc.*, 1907, **3**, 1),

who recalculated the experimental results of Knopp (*Z. physikal. Chem.*, 1904, **48**, 97), Steiner (*Wied. Ann.*, 1894, **52**, 275), and Muller (*Z. physikal. Chem.*, 1912, **81**, 483) on the solubility of gases in aqueous solutions of sucrose, potassium chloride, etc., and showed that the solubility of hydrogen, nitrogen, and oxygen in these solutions was considerably less than might be expected from their known water content. He suggested that this lowering of solubility might be accounted for by assuming that some of the water was attached to the solute as water of hydration and thereby removed from its rôle of solvent, and that the lowering of solubility afforded a direct measure of this "fixed" water. Philip and Bramley (*J.*, 1915, **107**, 377, 1831) employed the distribution method to measure this effect, while H. E. Armstrong and his collaborators (*Proc. Roy. Soc.*, 1906, **78**, A, 272; 1907, **79**, A, 576, 579, 586; 1908, **81**, A, 102; 1912, **87**, A, 582; *J.*, 1911, **99**, 349, 371), by investigating the velocity of reactions such as the inversion of sucrose and the hydrolysis of methyl acetate by dilute acids, alone and in presence of their salts, calculated the hydration of the salt by estimating the amount of water required to be added to the solution in order to restore the velocity coefficient to its original value. In view of the approximate agreement of the results obtained by these methods, it was thought desirable to make a further study of the problem by the distribution method, which is the most convenient.

The experimental conditions desirable on theoretical grounds were laid down by Philip and Bramley (*loc. cit.*), but these have been modified in that a system was sought in which the distributed solute (a) can be estimated quickly, preferably by simple titration, (b) is miscible in all proportions with both the aqueous and the non-aqueous phase, and (c) is distributed equally between the two solvent phases. Only one such system could be found, *viz.*, acetic acid distributed between water and amyl alcohol, which had been investigated by Herz and Fischer (*Ber.*, 1904, **37**, 4746; 1905, **38**, 1138). The distribution coefficient was found to vary somewhat with the source of the alcohol (usually about the figure 0.96) and to be independent of the concentration of the acetic acid when tested on the following systems: amyl alcohol and (a) water, (b) 2*N*-sodium chloride, (c) *N*-potassium nitrate, (d) 0.25 *N*-sucrose, and also of the time, showing that esterification in the alcohol phase did not take place. The objections to this system are (a) the two solvents are slightly miscible with each other, (b) some salts are not insoluble in amyl alcohol, (c) iodides are decomposed by the acetic acid and the liberated iodine dissolves in the alcohol, and (d) acetic acid cannot be estimated by titration in presence of

ammonium salts. Complete immiscibility is, however, not essential when the distribution coefficient is approximately unity, and other methods can be applied in the case of the soluble lithium, magnesium, and calcium salts and of ammonium salts.

If  $d_1$  and  $d_2$ , and  $C_1$  and  $C_2$ , are respectively the densities and distribution coefficients of water and a salt solution of normality  $n$ , the total weight of water per litre of solution is  $1000d_2 - nE$  ( $E$  being the equivalent weight of the salt). The weight of free water is taken to be  $1000d_1 \cdot C_1/C_2$  ( $d_1 = 0.99707$ ), and consequently the weight of water attached to  $n$  gram-equivalents of the salt is  $1000d_2 - nE - 1000d_1C_1/C_2$  and the apparent equivalent hydration

$$H = 1000(d_2 - C_1d_1/C_2)/18n - E/18.$$

This calculation assumes the solvents to be completely immiscible, the quantity of acetic acid (actually 1 c.c. of acid per 200 c.c. of solvents) to be negligible, and the indicating substance (acetic acid) to be insoluble in the salt whose hydration is being determined.

In Table I are the results of the first experiments, with sucrose. The apparent molecular hydration,  $H$ , increases with dilution until

TABLE I.

$n$ .	$d$ .	$C_1$ .	$C_2$ .	$H$ .	$n$ .	$d$ .	$C_1$ .	$C_2$ .	$H$ .
2N	1.2532	0.9870	2.061	2.7	N/4	1.0300	0.9227	1.019	5.0
		0.9625	2.030	2.7			0.9625	1.042	5.2
N	1.1270	0.9780	1.376	4.2	N/5	1.0234	0.9663	1.029	5.1
		0.9625	1.360	4.3			0.9663	1.030	5.6
N/2	1.0623	0.9625	1.135	5.2	N/7	1.0153	0.9663	1.011	5.5
		0.9623	1.133	4.9			0.9659	1.012	6.1
N/3	1.0407	0.9663	1.072	4.8	N/10	1.0103	0.9623	0.9933	5.6
		0.9659	1.073	4.9			0.9623	0.9954	6.5

a value of 5 to 6 molecules of water is obtained. The method of estimating  $H$  is by difference, and the experimental error increases rapidly as the fraction of "fixed" water decreases, i.e., as the dilution increases; in the case of sucrose a steady value is not indicated until a dilution is reached where the experimental error becomes appreciable, nevertheless the average value so obtained is in good agreement with that deduced from the osmotic properties of sucrose solutions.

Table II gives the results obtained for all the salts investigated, and Table IIa summarises those for the alkali metals.

In every case except the sulphates, a reasonably constant value of  $H$  was obtained, usually over the range  $N - N/10$ . The values in the column headed  $H(\text{ex.})^*$  are those which might be ascribed

\* Where the values of  $H$  over the range  $N - N/4$  are reasonably constant,  $H(\text{ex.})$  is taken as the average. Where  $H$  is large and the maximum value is not reached at normal concentration, e.g.,  $\text{LiBr}$ ,  $\text{LiBrO}_3$ , less weight is attached to this determination.



TABLE II.

Conc. (N.).	$d_2$ .	$C_1$ . LiCl.	$C_2$ .	$H$ .	Conc. (N.).	$d_2$ .	$C_1$ . LiBrO <sub>3</sub> .	$C_2$ .	$H$ .
1.516	1.0332	0.9526	1.2990	8.7	0.830	1.0809	0.9412	1.0962	7.5
1.0	1.0214	0.9526	1.1714	9.3	0.415	1.0392	0.9412	1.0143	7.75
0.5	1.0095	0.9526	1.0052	9.8	0.2075	1.0180	0.9412	0.9774	7.95
0.25	1.0034	0.9526	1.0006	9.75	0.083	1.0058	0.9412	0.9527	6.4
0.1	0.9995	0.9526	0.9698	8.8			NaBrO <sub>3</sub> .		
		NaCl.			1.0	1.1122	0.9632	1.1350	6.4
2.0	1.0794	0.9780	1.3660	6.9	0.5	1.0550	0.9632	1.0437	6.6
1.0	1.0380	0.9424	1.1150	7.0	0.25	1.0260	0.9632	1.0021	6.6
0.5	1.0180	0.9526	1.0331	8.0	0.1	1.0089	0.9632	0.9770	6.0
0.25	1.0078	0.9600	1.0006	8.1			KBrO <sub>3</sub> .		
0.1	1.0013	0.9628	0.9759	6.5	0.25	1.0290	0.9227	0.9405	2.0
		KCl.					LiIO <sub>3</sub> .		
2.0	1.0872	0.9820	1.1940	3.3	0.9927	1.1506	0.9227	1.1106	7.9
1.0	1.0427	0.9600	1.0534	3.3	0.4963	1.0745	0.9412	1.0241	7.6
0.5	1.0206	0.9424	0.9868	3.5	0.2482	1.0360	0.9227	0.9613	7.6
0.25	1.0091	0.9600	0.9808	3.3	0.0993	1.0127	0.9227	0.9393	8.5
0.1	1.0019	0.9520	0.9605	3.3			NaIO <sub>3</sub> .		
		LiBr.			0.25	1.0400	0.9412	0.9700	5.1
1.232	1.0735	0.9410	1.1533	6.9	0.1	1.0141	0.9510	0.9616	4.5
0.616	1.0353	0.9410	1.0504	8.1			KIO <sub>3</sub> .		
0.308	1.0162	0.9410	0.9922	7.9	0.25	1.0414	0.9227	0.9376	1.5
0.1232	1.0047	0.9410	0.9600	7.5			$\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub> .		
		NaBr.			2.0	1.1150	0.9780	1.4160	7.9
2.0	1.1503	0.9520	1.3024	6.0	1.0	1.0572	0.9780	1.1370	7.2
1.0	1.0747	0.9520	1.1045	6.2	0.5	1.0283	0.9410	1.0020	6.3
0.5	1.0360	0.9600	1.0343	6.4	0.25	1.0134	0.9410	0.9650	5.2
0.25	1.0165	0.9526	0.9892	6.8	0.1	1.0043	0.9410	0.9443	2.0
0.1	1.0045	0.9526	0.9663	6.3			$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub> .		
		KBr.			1.0	1.0638	0.9780	1.0570	3.0
2.0	1.1623	0.9520	1.1030	1.8	0.5	1.0310	0.9410	0.9661	1.8
1.0	1.0802	0.9520	1.0240	1.9	0.25	1.0137	0.9410	0.9491	0.8
0.5	1.0394	0.9520	0.9861	1.9			MgCl <sub>2</sub> .		
0.25	1.0181	0.9520	0.9687	1.9	2.260	1.0790	0.9424	1.4567	16.0
0.1	1.0052	0.9520	0.9582	1.5	1.130	1.0389	0.9424	1.1983	19.6
		LiNO <sub>3</sub> .			0.565	1.0183	0.9424	1.0632	21.0
0.900	1.0322	0.9410	1.0156	2.9	0.2825	1.0077	0.9424	0.9998	19.4
0.450	1.0147	0.9410	0.9820	3.5	0.113	1.0013	0.9424	0.9615	18.4
0.225	1.0062	0.9410	0.9592	3.1			CaCl <sub>2</sub> .		
0.090	1.0006	0.9410	0.9478	2.8	2.186	1.0924	0.9510	1.4374	15.8
		NaNO <sub>3</sub> .			1.093	1.0458	0.9510	1.1804	18.6
2.0	1.1040	0.9526	1.1032	2.0	0.546	1.0216	0.9400	1.0403	18.4
1.0	1.0518	0.9600	1.0266	1.9	0.273	1.0095	0.9510	1.0050	18.9
0.5	1.0247	0.9526	0.9815	1.6	0.109	1.0020	0.9510	0.9735	22.4
0.25	1.0113	0.9600	0.9740	1.6			SrCl <sub>2</sub> .		
0.1	1.0028	0.9600	0.9625	1.6	2.0	1.1369	0.9510	1.4052	15.8
		KNO <sub>3</sub> .			1.0	1.0679	0.9510	1.1690	18.6
1.0	1.0574	0.9600	0.9581	-2.4	0.5	1.0320	0.9510	1.0514	19.0
0.5	1.0276	0.9600	0.9559	-2.6	0.25	1.0150	0.9510	0.9980	18.8
0.25	1.0131	0.9520	0.9497	-2.6	0.1	1.0044	0.9510	0.9713	21.9
0.125	1.0044	0.9520	0.9506	-3.0			BaCl <sub>2</sub> .		
		NaClO <sub>3</sub> .			2.0	1.1740	0.9632	1.3323	13.6
2.0	1.1335	0.9632	1.2150	3.6	1.0	1.0869	0.9600	1.1387	15.8
1.0	1.0662	0.9632	1.0758	3.7	0.5	1.0424	0.9780	1.0630	16.2
0.5	1.0319	0.9632	0.9736	3.7	0.25	1.0198	0.9632	1.0036	16.3
0.25	1.0148	0.9632	0.9880	3.7	0.1	1.0062	0.9632	0.9760	16.1
0.1	1.0044	0.9632	0.9716	2.9			MgBr <sub>2</sub> .		
		KClO <sub>3</sub> .			1.7624	1.1302	0.9227	1.2845	15.9
0.25	1.0161	0.9526	0.9585	-1.2	0.8812	1.0641	0.9227	1.0960	18.2
0.1	1.0048	0.9526	0.9554	-0.9	0.4406	1.0308	0.9227	1.0090	19.8
					0.2203	1.0140	0.9227	0.9623	19.0
					0.0881	1.0040	0.9227	0.9402	21.6

TABLE II (continued).

Conc. (N.).	$d_2$ .	$C_1$ .	$C_2$ .	$H$ .	Conc. (N.).	$d_2$ .	$C_1$ .	$C_2$ .	$H$ .
CaBr <sub>2</sub> .					Ca(NO <sub>3</sub> ) <sub>2</sub> .				
2.148	1.1706	0.9424	1.3282	12.8	2.18	1.1243	0.9400	1.1448	6.5
1.074	1.0848	0.9424	1.1323	15.3	1.09	1.0618	0.9400	1.0346	6.8
0.537	1.0412	0.9424	1.0365	16.8	0.545	1.0292	0.9400	0.9850	6.7
0.268	1.0193	0.9424	0.9857	16.2	0.2725	1.0130	0.9400	0.9619	6.7
0.1074	1.0063	0.9424	0.9603	17.9	0.109	1.0036	0.9400	0.9480	6.2
SrBr <sub>2</sub> .					Sr(NO <sub>3</sub> ) <sub>2</sub> .				
2.0	1.2027	0.9400	1.2737	12.2	1.9736	1.1297	0.9510	1.1495	5.4
1.0	1.1008	0.9400	1.1011	14.0	0.9868	1.0775	0.9510	1.0373	6.7
0.5	1.0493	0.9424	1.0264	16.0	0.4939	1.0377	0.9510	0.9923	6.8
0.25	1.0231	0.9400	0.9795	15.7	0.2969	1.0176	0.9510	0.9715	7.0
0.1	1.0078	0.9400	0.9536	14.0	0.09868	1.0057	0.9510	0.9578	6.0
BaBr <sub>2</sub> .					Ba(NO <sub>3</sub> ) <sub>2</sub> .				
2.0	1.2510	0.9424	1.2400	10.9	0.5	1.0494	0.9510	0.9825	4.2
1.0	1.1251	0.9424	1.0900	12.7	0.25	1.0233	0.9510	0.9660	4.0
0.5	1.0615	0.9424	1.0146	13.6	0.1	1.0076	0.9510	0.9565	3.5
0.25	1.0293	0.9424	0.9777	13.4	MgSO <sub>4</sub> .				
0.1	1.0100	0.9424	0.9572	15.0	2.0	1.1104	0.9400	1.4855	20.0
Mg(NO <sub>3</sub> ) <sub>2</sub> .					1.0	1.0552	0.9400	1.1555	20.4
2.02	1.0993	0.9400	1.1448	7.2	0.5	1.0266	0.9400	1.0287	19.0
1.01	1.0489	0.9400	1.0394	8.0	0.25	1.0121	0.9400	0.9788	17.6
0.505	1.0231	0.9400	0.9889	8.3	0.1	1.0035	0.9400	0.9519	14.4
0.2525	1.0100	0.9400	0.9634	8.1					
0.101	1.0023	0.9400	0.9467	5.3					

to the salt from these experimental results alone, whilst under  $H$  are the most probable values for the apparent molecular hydration. Where the values in the two columns differ, the explanation is usually to be found in the solubility of the salt in the alcohol phase; the evidence upon which the final figure is based will appear in later sections. All previous work on hydration suggests that this

TABLE IIA.

Salt.	2N.	N.	N/2.	N/4.	N/10.	$H$ (ex.).*	$H$ .
LiCl	8.7	9.3	9.8	9.75	8.8	9.8	10.5
NaCl	6.9	7.6	8.0	8.1	6.5	8.0	7.9
KCl	3.3	3.3	3.5	3.3	3.3	3.4	3.4
LiBr	—	6.9	8.1	7.9	7.5	8.0	9.0
NaBr	6.0	6.2	6.4	6.8	6.3	6.6	6.4
KBr	1.8	1.9	1.9	1.9	1.5	1.9	1.9
LiNO <sub>3</sub>	—	2.9	3.5	3.1	2.8	3.4	4.4
NaNO <sub>3</sub>	2.0	1.9	1.6	1.6	1.6	1.8	1.8
KNO <sub>3</sub>	—	2.4	2.6	2.6	3.0	2.6	2.7
LiClO <sub>3</sub>	—	—	—	—	—	—	6.3
NaClO <sub>3</sub>	3.6	3.7	3.7	3.7	2.9	3.7	3.7
KClO <sub>3</sub>	—	—	—	1.2	0.9	1.0	0.8
LiBrO <sub>3</sub>	—	7.5	7.75	7.95	6.4	7.8	9.2
NaBrO <sub>3</sub>	—	6.4	6.6	6.6	6.0	6.6	6.6
KBrO <sub>3</sub>	—	—	—	2.0	—	2.0	2.1
LiIO <sub>3</sub>	—	7.9	7.6	7.6	8.5	7.7	7.7
NaIO <sub>3</sub>	—	—	—	5.1	4.5	5.1	5.1
KIO <sub>3</sub>	—	—	—	1.5	—	1.5	0.6
Na <sub>2</sub> SO <sub>4</sub>	7.9	7.2	6.3	5.2	2.0	—	—
K <sub>2</sub> SO <sub>4</sub>	—	3.0	1.8	0.8	—	—	—

quantity is not independent of the salt concentration, but the results now obtained (with the one exception) do not support this view, and, whilst it cannot be shown from them alone whether or not the constant value is retained as the dilution is still further increased, it will be convenient, for the time being, to regard these as fixed values. The sulphates are anomalous, the values of  $H$  actually decreasing on dilution. This may be due to the appearance and subsequent dissociation of intermediate ions of the type  $\text{KSO}_4$ , or to some idiosyncrasy of the sulphate ion; salts of the type  $\text{BaCl}_2$  and  $\text{Sr}(\text{NO}_3)_2$  behave in the normal way.

Potassium bromate and iodate are only sparingly soluble salts, consequently their hydration could not be determined with accuracy. Potassium nitrate and potassium chlorate both gave constant negative values for  $H$ . Analysis of the figures brings out the interesting fact that *the difference between the apparent molecular hydration of a sodium and a potassium salt is independent of the anion, hydration thus being an additive property* (Table III).

TABLE III.

	Cl.	Br.	$\text{NO}_3$ .	$\text{ClO}_3$ .	$\text{BrO}_3$ .	$\text{IO}_3$ .
Na	8.0	6.6	1.8	3.7	6.6	5.1
K	3.4	1.9	-2.6	-1.0	2.0	(1.5)
Diff.	4.6	4.7	4.4	4.7	4.6	(3.6)

The average value for the Na-K difference is 4.6 mols.  $\text{H}_2\text{O}$ . The determination of the corresponding Li-Na difference presented some difficulty, due to the solubility of lithium salts in amyl alcohol. Of those examined, the iodate alone was insoluble, so the difference (2.6 mols.  $\text{H}_2\text{O}$ ) depends on only one determination; moreover, sodium iodate is a sparingly soluble salt and the most concentrated solution available was  $N/4$ , hence the value  $H = 5.1$  for this salt is not known with the usual accuracy. Nevertheless, the difference value of 2.6 is probably not greatly in error; the hydration values for the other lithium salts tabulated in column  $H$  (Table II) are obtained by adding 2.6 to the hydration number of the corresponding sodium salts.

Table IV gives a summary of the values of  $H$  for the salts of the alkaline earths. The magnesium and calcium salts dissolved in the amyl alcohol and in each case the numbers in column  $H$  (ex.) are too small, but good values were obtained for the strontium and barium salts; the chlorides and bromides are heavily hydrated and hence the maximum value is in some cases not obtained until a dilution somewhat greater than normal is reached.

Table V indicates that hydration is additive in these salts also, and Table VI that the chloride-nitrate difference is common to both series.

TABLE IV.

Salt.	2N.	N.	N/2.	N/4.	N/10.	H (ex.).	H.
MgCl <sub>2</sub>	16.0	19.6	21.0	19.4	18.4	20.0	24.8
CaCl <sub>2</sub>	15.8	18.6	18.4	18.9	22.4	18.4	20.6
SrCl <sub>2</sub>	15.8	18.6	19.0	18.8	21.9	18.8	18.8
BaCl <sub>2</sub>	13.6	15.8	16.2	16.3	13.1	16.2	16.2
MgBr <sub>2</sub>	15.9	18.2	19.8	19.0	21.6	19.2	21.8
CaBr <sub>2</sub>	12.8	15.3	16.8	16.2	17.9	16.3	17.6
SrBr <sub>2</sub>	12.2	14.0	16.0	15.7	14.0	15.9	15.8
BaBr <sub>2</sub>	10.9	12.7	13.6	13.4	15.0	13.5	13.2
Mg(NO <sub>3</sub> ) <sub>2</sub>	7.2	8.0	8.3	8.1	5.3	8.1	12.8
Ca(NO <sub>3</sub> ) <sub>2</sub>	6.5	6.8	6.7	6.7	6.2	6.75	8.6
Sr(NO <sub>3</sub> ) <sub>2</sub>	5.4	6.7	6.8	7.0	6.0	6.7	6.8
Ba(NO <sub>3</sub> ) <sub>2</sub>	—	—	4.2	4.0	3.5	4.1	4.1
MgSO <sub>4</sub>	20.0	20.4	19.0	17.6	14.4	—	—

TABLE V.

	Cl.	Br.	NO <sub>3</sub> .
Sr	18.8	15.9	6.7
Ba	16.2	13.5	4.1
Diff.	2.4	2.4	2.6

TABLE VI.

	Na.	K.	$\frac{1}{2}$ Sr.	$\frac{1}{2}$ Ba.
	8.0	3.4	9.4	8.1
	1.8	-2.6	3.35	2.05
Diff.	6.2	6.0	6.05	6.05

*Negative Hydration.*

The salts possessing negative hydration values are the chlorates and nitrates of potassium and presumably also of ammonium, rubidium, and caesium. Since, so far as the additive nature of hydration is concerned, these salts are apparently normal, it is probable that this phenomenon is not an abnormality, but merely an extreme example of some property common to all strong electrolytes. In this particular case, the negative hydration is indicated by the fact that solutions of these salts exert a greater solvent power upon acetic acid than does pure water. An obvious explanation is that some measure of combination takes place between the salt and acetic acid, but several arguments may be raised against this. One of these (and others will appear later) is that the negative hydration, or, from the point of view of this explanation, the extent of combination between the two substances is independent of the concentration of both the potassium nitrate and the acetic acid over a wide range of concentration. The increased solvent power of potassium nitrate solutions is not confined to acetic acid alone; reference to the papers of Rothmund (*Z. physikal. Chem.*, 1900, **33**, 401), Biltz (*ibid.*, 1903, **43**, 41), Bray and Winninghoff (*J. Amer. Chem. Soc.*, 1911, **33**, 1663), and Glasstone and Saunders (*J.*, 1923, **123**, 2134) shows that the property extends over a very wide range of compounds, including the particularly interesting case of lead nitrate (Glasstone and Saunders), which contains a common ion. Moreover, whereas the ordinary process

of hydration produces a concentrating effect upon other constituents of an aqueous solution, evidence is not lacking that these "negatively hydrated" salts actually produce a *diluting effect*, a property which has been noticed by Rennie, Higgin, and Cooke (J., 1908, 93, 1162), Armstrong and Watson (*Proc. Roy. Soc.*, 1907, 79, A, 586), Harned (*J. Amer. Chem. Soc.*, 1918, 40, 1461), and Walton (*Z. physikal. Chem.*, 1904, 47, 185).

Several explanations of these anomalies are to be found in the above papers, but in seeking a general interpretation which will cover these and other properties of solutions of strong electrolytes the possibility was considered that the anions and cations might react with the solvent in fundamentally different ways. All the published work on hydration of strong electrolytes agrees on two points: (1) if cations are arranged in the order of diminishing hydration, the caesium ion occupies the lowest position, and (2) if the anions are so arranged, the chloride ion occupies the position of maximum hydration; this, together with the definite proof advanced by Washburn (*J. Amer. Chem. Soc.*, 1915, 37, 694) that the least hydrated cation (caesium) carries measurably more water than the (presumably) most heavily hydrated anion (chloride), suggests at once that anions are not hydrated, but possess properties which in certain cases are sufficiently developed to over-compensate the hydration effect of the cation.

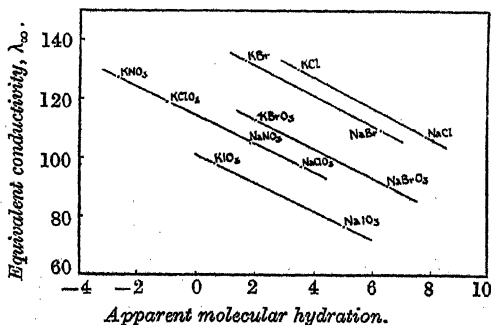
When acetic acid is in equilibrium both with water and with amyl alcohol, its activity in each phase must be the same, and (if the solution is sufficiently dilute) proportional to its mole-fraction, which in the aqueous phase is assumed to depend on the "association factor" of water. If the mole-fraction (activity) of the acetic acid in the aqueous phase is increased by the removal of water as water of hydration, some of the acid will escape into the alcohol phase until equilibrium is re-established. Alternatively, if the association factor of water is decreased by any means whatsoever, the mole-fraction of the acetic acid will decrease and can only be restored by transference of the acid from the alcohol to the water phase. The suggestion is made, therefore, that whilst cations are invariably hydrated, probably as a result of the positive field (the intensity of which decreases as the ionic radius increases) round the ion and a stray field round the water molecule, anions are not hydrated but in all cases exert (in greater or less degree) a depolymerising action on the associated solvent, resulting in a shift of the equilibrium  $(\text{H}_2\text{O})_3 \rightleftharpoons (\text{H}_2\text{O})_2 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2\text{O}$  towards the right. The properties of solutions of strong electrolytes are thus to a large degree determined by the relative magnitudes of these two rival processes.

An action such as the above, which increases the effective mole-fraction of the water, will produce a species of water molecule which alone is found in the vapour phase; hence aqueous solutions of negatively hydrated salts should have abnormally high vapour pressures (compare Washburn, *J. Amer. Chem. Soc.*, 1910, **32**, 653, 1636; Washburn and MacInnes, *ibid.*, 1911, **33**, 1686; Bousfield, *Trans. Faraday Soc.*, 1919, **15**, 47; Glasstone and Saunders, *loc. cit.*; Sidgwick and Ewbank, *J.*, 1924, **125**, 2273).

*Hydration and the Equivalent Conductivity at Infinite Dilution.*

Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, A, 348) suggested that "about every ion moves an atmosphere of the solvent the dimensions of which are determined by the characteristics of the ion,

FIG. 1.



and the electrolytic resistance of an ion is a frictional resistance that increases with the dimension of the atmosphere"; consequently a quantitative relationship may be expected between  $\lambda_{\infty}$  and the hydration of the kations.\* In order to correlate these properties, let it be assumed that  $H$  is independent of concentration up to infinite dilution. This assumption is not unreasonable in view of the facts presented in this paper, and further, it leads to conclusions which are supported by considerations based on the constancy of  $H$  over the experimental range  $N - N/10$  only.

If the apparent molecular hydrations of the alkali chlorides are plotted against the equivalent conductivities at infinite dilution, the points lie on a smooth curve, which is slightly concave towards the origin. The shape of the curve is determined by the properties ( $\lambda_{\infty}$  and  $H$ ) of the kations, and its position on the diagram by the equivalent conductivity of the anion. In a similar diagram drawn for the salts of a common kation, the points lie irregularly

\* The hypothesis cannot be true universally if anions are not hydrated.

and can only be joined by a zig-zag line. This dissimilarity supports the hypothesis that anions and kations behave towards the solvent in different ways.

The curvature of the lines relating  $\lambda_{\infty}$  and  $H$  for the alkali metals (so far as their hydrations are known) is so slight that the purpose of the diagram is served equally well by plotting the values for the sodium and potassium salts only and joining the points by straight lines (Fig. 1). Two points of interest, which will be encountered again later, become evident: (a) the nitrates and chlorates fall on one line, and (b) the sequence of the curves for the bromates, chlorates, and iodates is unexpected.

#### *Hydration of Strong Electrolytes and the Viscosity of their Aqueous Solutions.*

Strong electrolytes may be divided into two classes according to their effect on the viscosity of water. The first (and smaller) class consists of the salts of the heavier alkali metals the aqueous solutions of which at the ordinary temperature have viscosities lower than that of the solvent. With increasing concentration, the viscosity falls at first to a minimum and then increases to a value which, in the case of very soluble salts, may exceed the viscosity of water. At higher temperatures the minimum becomes less marked and finally disappears, the solution then behaving as solutions of electrolytes of the second (and larger) class, the viscosities of which are always greater than that of water.

Many unsatisfactory and conflicting theories have been put forward to explain the negative viscosity ( $\eta/\eta_0 - 1$  being negative) of some salt solutions, *e.g.*, by Euler (*Z. physikal. Chem.*, 1898, 25, 536), Wagner (*ibid.*, 1903, 46, 871), Jones and Veazey (*Amer. Chem. J.*, 1907, 37, 405), and Taylor (*Proc. Roy. Soc. Edin.*, 1907, 28, 461).

Getman (*J. Chim. Phys.*, 1907, 5, 344; *J. Amer. Chem. Soc.*, 1908, 30, 721, 1077) ascribed negative viscosity at least partly to association of the solvent (potassium iodide in non-associated solvents having a positive viscosity), Bousfield (*J.*, 1915, 107, 1797) pointed out that "the viscosity of dilute aqueous solutions cannot be theoretically treated except in conjunction with the effect of the peculiar constitution of water," and Rabinowitsch (*J. Amer. Chem. Soc.*, 1922, 44, 954) showed, from theoretical considerations, that whilst hydration of ions can account for an increased viscosity, depolymerisation of the solvent alone supplies a rational explanation of the negative viscosity of some salt solutions.

When the kation is only slightly hydrated and the non-hydrated anion is small, or efficient in depolymerising the solvent, the effect

of the anion predominates, and the viscosity of the solution will be negative; but with increasing salt concentration, and therefore increasing depolymerisation, the average size of the water molecules becomes smaller, and hence the tendency of the kation to increase the viscosity will become more marked, eventually accounting for the minimum value and subsequent increase in the viscosity. Increase of temperature causes depolymerisation and consequently the disappearance of the minimum in the curve, the solvent functioning at higher temperatures as if it consisted only of simple molecules or complexes incapable of easy depolymerisation.

FIG. 2.

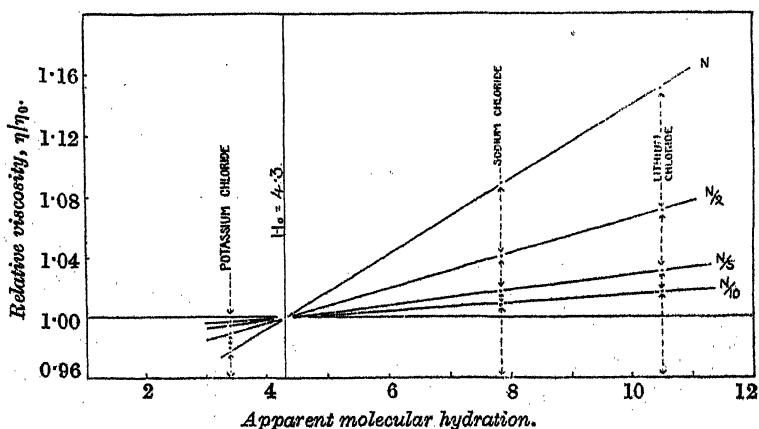


Fig. 2 shows the relation between the hydration of the alkali chlorides and the relative viscosity\* of their solutions. If the latter is greater than unity, it is at all concentrations a linear function of the apparent molecular hydration of the salt; if less than unity, this relationship holds up to approximately semi-normal concentration. The straight lines in Fig. 2 all pass through a point where  $\eta/\eta_0 = 1$  and  $H = 4.3$ . If an alkali chloride had this hydration value of 4.3, all disturbing influences would exactly compensate one another and the viscosity of its solutions at all concentrations would be the same as that of pure water. The relative viscosities of solutions of the alkali chlorides are proportional to the differences between their apparent molecular hydrations and this "zero" value, which may be denoted by  $H_0$ . The point of origin  $\eta/\eta_0 = 1$ ,  $H = 4.3$  is independent both of the concen-

\* Except where otherwise stated, the accurate viscosity measurements of Gruneisen (*Wiss. Abhandl. Physikal.-Tech. Reichsanst.*, 1905, 4, 239), and the collected data of Noyes and Falk (*J. Amer. Chem. Soc.*, 1912, 34, 463) have been used.



tration and of the nature of the kation; it is determined by the anion, of which it is a specific property. The viscosities of these solutions depend, therefore, on (a) the value of  $H_0$ , which is fixed by the anion, (b) the hydration of the salt (determined largely by the kation), and (c) the concentration of the solution.

Many empirical equations have been proposed connecting the viscosities and the concentrations of solutions of strong electrolytes. The simplest of these (Arrhenius, *Z. physikal. Chem.*, 1887, **1**, 284),

$$\log \eta/\eta_0 = \theta c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $\theta$  is a constant varying from salt to salt and  $c$  is the number of gram-molecules per litre, holds with considerable accuracy over a wide range of concentrations, provided the solutions are more viscous than water, whilst for solutions of negative viscosity its application is limited to dilutions greater than semi-normal. It is obvious from Fig. 2 that the constant  $\theta$  may be expressed in terms of the apparent molecular hydration,  $H$ , and a more general constant,  $K$ :

$$\theta = K(H - H_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence 
$$\log \eta/\eta_0 = Kc(H - H_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a general equation which has the same applicability as that of Arrhenius. In Table VII,  $K$  is evaluated for the alkali chlorides, the calculated values of  $\eta/\eta_0$  being then obtained from the equation

$$\log \eta/\eta_0 = 0.01c(H - 4.3) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

TABLE VII.

LiCl. $H = 10.5$ .				NaCl. $H = 7.9$ .				KCl. $H = 3.4$ .			
c.	$\eta/\eta_0$ .	$K$ .	$\eta/\eta_0$ (calc.).	$\eta/\eta_0$ .	$K$ .	$\eta/\eta_0$ (calc.).	$\eta/\eta_0$ .	$K$ .	$\eta/\eta_0$ (calc.).	$\eta/\eta_0$ .	$\eta/\eta_0$ (calc.).
1.0N	1.150	0.0098	1.153	1.086	0.0101	1.085	0.9820	(0.0088)	0.9785		
0.5N	1.072	0.0097	1.074	1.041	0.0099	1.042	0.9898	0.0097	0.9897		
0.2N	1.031	0.0107	1.029	1.0167	0.0101	1.0164	0.9959	0.0097	0.9958		
0.1N	1.016	0.0111	1.014	1.0086	0.0103	1.0082	0.9982	0.0097	0.9989		
0.05N	1.008	0.0109	1.007	1.0046	0.0110	1.004	0.9991	0.0096	0.9998		

Mean value of  $K = 0.01$ .

The figures in brackets in Tables VII and VIII refer to solutions for which  $\eta/\eta_0 - 1$  is negative, and of such concentrations that equation (1) is no longer applicable.

The corresponding diagram for the alkali nitrates closely resembles that for the chlorides, except that the origin of the curves has shifted to the value  $H_0 = 0$ ; however, the value of  $K$  (0.01) is the same (within the limits of experimental error), as will be seen from Table VIII.

TABLE VIII.

LiNO <sub>3</sub> . $H = 4.4$ .				NaNO <sub>3</sub> . $H = 1.8$ .				KNO <sub>3</sub> . $H = -2.7$ .			
c.	$\eta/\eta_0$ .	$K$ .	$\eta/\eta_0$ (calc.).	$\eta/\eta_0$ .	$K$ .	$\eta/\eta_0$ (calc.).	$\eta/\eta_0$ .	$K$ .	$\eta/\eta_0$ (calc.).	$\eta/\eta_0$ .	$K$ .
1.0N	1.1020	0.0094	1.1066	1.0540	0.0127	1.0423	0.9620	(0.0070)	0.9397		
0.5N	1.0503	0.0095	1.0520	1.0219	0.0104	1.0209	0.9754	(0.0083)	0.9694		
0.2N	1.0200	0.0096	1.0205	1.0082	0.0096	1.0084	0.9883	0.0095	0.9876		
0.1N	1.0112	0.0107	1.0102	1.0044	0.0102	1.0039	0.9841	0.0094	0.9969		

It is possible, therefore, that  $K$  may be a universal constant and the equation

$$\log \eta/\eta_0 = 0.01c(H - H_0) \quad . \quad . \quad . \quad (5)$$

a general one.

For the alkali iodates, which (with the exception of the lithium salt) are only sparingly soluble in water, the value of  $H_0$  (Table IX) has been calculated from equation (5) instead of being obtained by the graphical method. The average value is  $-5.5$ .

TABLE IX.

	c.	$\eta/\eta_0$ .	$H_0$ .	$\eta/\eta_0$ (calc.).
LiIO <sub>3</sub>	1.00N	1.3380	-4.9	1.3552
	0.20N	1.0620	-5.4	1.0627
	0.05N	1.0158	-5.7	1.0153
	0.025N	1.0086	-6.7	1.0076
	0.020N	1.0496	-5.4	1.0481
NaIO <sub>3</sub>	0.20N	1.0496	-5.4	1.0481
KIO <sub>3</sub>	0.20N	1.0270	-5.2	1.0285

The negative sign probably indicates that the iodate ion is sufficiently large of itself to increase the viscosity of water, an effect which is, of course, independent of its depolymerising action.

The values of  $H_0$  for the bromides (4.1) and chlorates (0.0) were similarly found. In the case of the bromates, owing to lack of data, new viscosity measurements were made ( $H_0 = 1.6$ ).

TABLE X.

LiBrO <sub>3</sub> . $H = 9.2$ .				NaBrO <sub>3</sub> . $H = 6.6$ .			
c.	$\eta/\eta_0$ .	$H_0$ .	$\eta/\eta_0$ (calc.).	c.	$\eta/\eta_0$ .	$H_0$ .	$\eta/\eta_0$ (calc.).
0.830N	1.154	1.7	1.156	1.0N	1.122	1.6	1.122
0.415N	1.076	1.6	1.075	0.5N	1.059	1.6	1.058
0.207N	1.036	1.8	1.037	0.25N	1.027	2.0	1.029
0.083N	1.014	1.5	1.015	0.1N	1.013	1.0	1.012

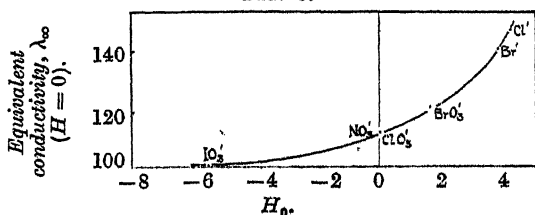
The values of  $H_0$  thus found are 4.3 for Cl, 4.1 for Br, 1.6 for BrO<sub>3</sub>, 0.0 for NO<sub>3</sub>, 0.0 for ClO<sub>3</sub>, and  $-5.5$  for IO<sub>3</sub>. The chlorates and nitrates form one system here as in Fig. 1 and the sequence of the curves in Fig. 1 is that of these  $H_0$  values. Fig. 3 shows the relation between the spacing of the curves in Fig. 1 as measured by the

value of  $\lambda_\infty$  at  $H = 0$ , and the values of  $H_0$ . This curve can be accurately described by the empirical equation

$$\lambda_\infty = 100 + 13.5 \times 1.327^H. \quad (6)$$

It indicates a lower limit for the position of the curves in Fig. 1, only slightly below that of the iodate curve. Moreover, the smooth curve in Fig. 3 is of some importance, for whereas the values of  $H_0$  are obtained from the viscosities of solutions over a concentration range similar to that available for the determination of hydration by the distribution method, the sequence and spacing of the curves in Fig. 1 depend on the application of these hydration values at infinite dilution. Fig. 3 therefore supplies some justification for extending the use of these hydration numbers to infinitely dilute solutions, since no serious error is thereby introduced. It must be mentioned, however, that "the viscosity concentration curve for all salts has a change of curvature at the dilute end in

FIG. 3.



the sense that the first particles of salt added have a greater effect in increasing, or a less effect in diminishing the viscosity of water than subsequent additions. The change in curvature is scarcely noticeable unless the curve is plotted on a large scale" (Applebey, J., 1910, 97, 2000; see also Grüneisen, *loc. cit.*).

Salts of the type  $\text{BaCl}_2$  can be treated in exactly the same way as those of the type  $\text{KCl}$ . By substituting the viscosity and apparent molecular hydration of barium chloride in equation (5), the value  $H_0 = 7.4$  is obtained. On the assumption that  $H_0$  is determined solely by the anion the value for a bivalent chloride might be expected to be 8.6. The agreement, therefore, is not unsatisfactory, and supports the assumption that  $K$  in equation (5) is a universal constant.\*

\* It appears not unlikely that the size of a (unhydrated) kation is less than that of an average water molecule; consequently some small part of the water of hydration may be needed to adjust this difference, whilst the remainder tends to increase the viscosity of salt solutions. Hence  $H_0$  for a bivalent chloride might be expected to be slightly less than twice the value for a univalent chloride, since, although the number of anions per molecule is doubled, that of the kations remains the same.

Having obtained  $H_0$  for these salts, it is possible to calculate, from the equation

$$\log \eta/\eta_0 = 0.01c(H - 7.4) \quad . \quad . \quad . \quad (7)$$

the values of  $H$  for magnesium chloride ( $H = 24.8$ ) and calcium chloride ( $H = 20.6$ ). Where the final value of  $H$  differs from the experimental value  $H$  (ex.), (i.e., for soluble salts), it is obtained (a) in Table IIA, from the additive property of hydration and (b) in Table IV, from this semi-empirical hydration-viscosity equation.

#### *Hydration of Strong Electrolytes and the Dilution Law.*

According to the theory here developed, the apparent molecular hydration,  $H$ , which represents the resultant of two opposing factors, viz., hydration of kations (decrease of the effective mole-fraction or activity of water) and depolymerisation by anions (increase of the effective mole-fraction or activity of water), may be applied to determine the effective mole-fraction of water and thus the corrected van 't Hoff factor,  $i$ .

Washburn (*Tech. Quart.*, 1908, 21, 373) has shown that the effective mole-fraction,  $n'$ , of the solute may be calculated from the freezing-point depression,  $\Delta t^\circ$ , by means of the equation

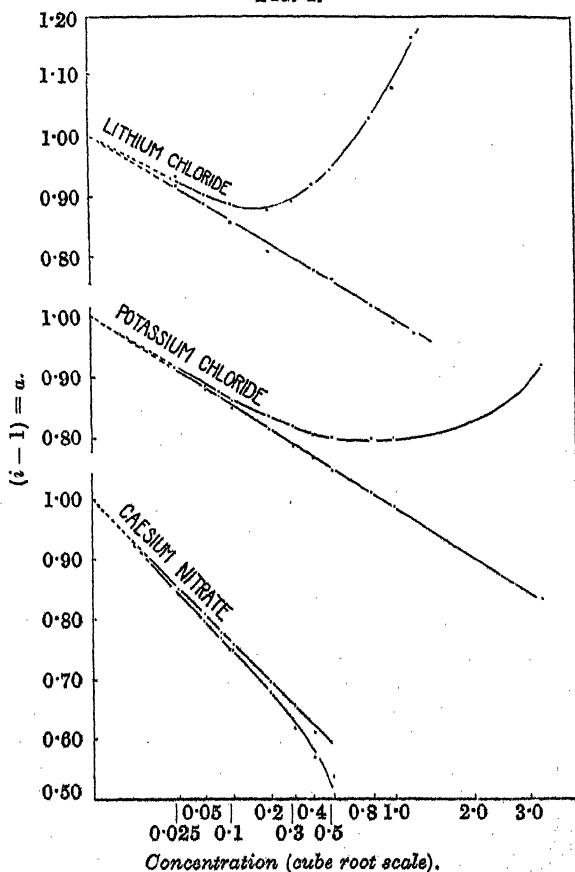
$$n' = 0.00969 (\Delta t - 0.00425 \Delta t^2) \quad . \quad . \quad . \quad (8)$$

This equation may be used for freezing-point depressions as large as  $7^\circ$ , and the mole-fraction is given with an accuracy equivalent to an experimental error of  $0.001^\circ$  in measuring  $\Delta t$ . Equation (8) may be equated to (a)  $ni/(ni + N)$  and (b)  $ni_c/(ni_c + N - Hn)$ , where  $n$  and  $N$  are the numbers of gram-molecules of solute and solvent, and  $i$  and  $i_c$  the uncorrected and corrected van 't Hoff factor, respectively.

van 't Hoff's factor is defined on the basis of the classical theory by the equation (for a uni-univalent salt)  $i = 1 + \alpha$ , where  $\alpha$  is the "degree of dissociation." Alternatively,  $(1 - \alpha)$  may be regarded simply as the "osmotic deficiency," i.e., the fraction by which the osmotic properties deviate from those required for an ideal solution of a completely dissociated salt. It was necessary, therefore, to review the recorded freezing-point depressions, more especially those referring to concentrated solutions where the hydration correction is considerable. Probably the most trustworthy measurements are those of Washburn and MacInnes (*loc. cit.*), who selected lithium chloride, potassium chloride, and caesium nitrate as being representative of the whole range of hydrated salts, lithium chloride being presumably the most and caesium nitrate the least heavily hydrated of the uni-univalent strong

electrolytes. In addition, the results of Noyes and Falk (*J. Amer. Chem. Soc.*, 1910, **32**, 1011), Jones and Pearce (*Amer. Chem. J.*, 1907, **38**, 683), Ponsot (*Ann. Chim. Phys.*, 1897, **10**, 79), de Coppet (*J. Physical Chem.*, 1904, **8**, 531; *Z. physikal. Chem.*, 1897, **22**, 239), Biltz (*Z. physikal. Chem.*, 1902, **40**, 185), Jahn (*ibid.*, 1904, **50**, 129; 1907, **59**, 31), Adams (*J. Amer. Chem. Soc.*, 1915, **37**,

FIG. 4.



481), Harkins and Hall (*ibid.*, 1916, **38**, 2658), Rodebush (*ibid.*, 1918, **40**, 1204), and Rivett (*Z. physikal. Chem.*, 1912, **80**, 546) have been used for the calculations, of which a selection is given in Table XI. In applying the hydration correction it was assumed that the hydration is (a) independent of the concentration and (b) has the same value at the freezing point as at 25°, the temperature at which the hydration determinations were made.



TABLE XI.

LiCl.  $H = 10.5$ .  $K = 0.31$ .

$n$ .	$\Delta t$ .	$\alpha$ .	$\alpha$ (corr.).	$K$ .	$\alpha$ (calc.).	%.
0.025	0.090°	0.939	0.9295	0.241	0.910	0.48
0.050	0.177	0.9075	0.889	0.300	0.8865	0.94
0.075	0.265	0.905	0.880	0.285	0.873	1.44
0.1	0.351	0.8925	0.857	0.308	0.857	1.91
0.2	0.694	0.875	0.804	0.335	0.820	3.82
0.3	1.049	0.893	0.781	0.327	0.794	5.73
0.4	1.416	0.924	0.778	0.301	0.773	7.65
0.5	1.791	0.947	0.763	0.303	0.756	9.55
0.8	2.966	1.031	0.721	0.302	0.714	15.3
1.0	3.792	1.083	0.690	0.310	0.690	19.1

KCl.  $H = 3.4$ .  $K = 0.32$ .

0.025	0.089	0.917	0.914	0.294	0.907	0.15
0.050	0.175	0.886	0.880	0.326	0.853	0.31
0.075	0.262	0.878	0.870	0.309	0.869	0.46
0.1	0.345	0.8605	0.849	0.325	0.852	0.62
0.2	0.680	0.837	0.814	0.318	0.814	1.24
0.3	1.009	0.820	0.787	0.318	0.787	1.86
0.4	1.335	0.805	0.765	0.317	0.766	2.48
0.5	1.658	0.802	0.746	0.325	0.747	3.10
0.8	2.635	0.798	0.710	0.313	0.705	4.92
1.0	3.287	0.801	0.691	0.309	0.680	6.20
1.989	6.46	0.791	0.583	0.331	0.600	11.8 †
3.30 *	11.10	0.922	0.535	0.312	0.527	20.2 ‡

CsNO<sub>3</sub>.  $H = 3.3$ .  $K = 0.52$ .

0.025	0.086	0.833	0.851	0.510	0.848	-0.15
0.05	0.168	0.807	0.812	0.510	0.809	-0.30
0.075	0.247	0.774	0.783	0.514	0.781	-0.45
0.1	0.352	0.753	0.763	0.511	0.759	-0.60
0.2	0.622	0.680	0.700	0.513	0.696	-1.2
0.3	0.897	0.618	0.647	0.527	0.652	-1.8
0.4	1.160	0.571	0.608	0.532	0.617	-2.4
0.5 *	1.419	0.539	0.585	0.531	0.588	-3.0

Washburn's values, except where marked † (Kistiakowski) and ‡ (de Coppet).

\* Cryohydric concentration.

atively, if any departure from the law is involved, not one but two changes in curvature would be necessary in order that the osmotic deficiency should not have a finite value at infinite dilution.

The freezing-point measurements of Adams (*loc. cit.*) and Hovorka and Rodebush (*J. Amer. Chem. Soc.*, 1925, 47, 1614) apply to dilute solutions, and are of a high order of accuracy, the former having been used to establish the freezing-point laws of Lewis and Linhart and of Brønsted. In Table XII their values of  $\alpha_c$  are compared with the calculated values:  $s$  = g.-mol. of salt in 1000 g. of water.

The figures for potassium chloride agree (within the limits of experimental error) with one another and with the calculated values, but those for the nitrates show considerable divergences

TABLE XII.

<i>s.</i>		0.001	0.002	0.005	0.01	0.02	0.05	0.1
$(1-a) = 0.32\sqrt{n.}$		0.968	0.960	0.945	0.931	0.914	0.883	0.852
KCl. Adams.		—	0.969	0.961	0.942	0.920	0.883	0.851
" H. & R.		0.962	—	0.956	0.933	—	—	—
" W.		—	—	—	—	—	0.880	0.849
KNO <sub>3</sub> . Adams.		—	0.967	0.958	0.938	0.910	0.853	0.797
CsNO <sub>3</sub> . H. & R.		0.966	—	0.950	0.934	—	—	—
" W.		—	—	—	—	—	0.812	0.763
$(1-a) = 0.52\sqrt{n.}$		0.948	0.934	0.911	0.888	0.859	0.808	0.759

TABLE XIII.

NaCl.  $H = 7.85$ .  $K = 0.32$ .

<i>n.</i>	$\Delta t.$	<i>a.</i>	$\alpha$ (corr.).	<i>K.</i>	$\alpha$ (calc.).	%.
0.005	0.01815°	0.953	0.952	0.281	0.945	0.07
0.01	0.036	0.938	0.936	0.297	0.931	0.14
0.02	0.0714	0.921	0.916	0.310	0.912	0.28
0.05	0.176	0.894	0.881	0.323	0.881	0.71
0.10	0.348	0.876	0.850	0.323	0.850	1.42
0.1168	0.406	0.875	0.8435	0.320	0.8435	1.66
0.235	0.808	0.859	0.797	0.329	0.802	3.32*
0.434	1.449	0.856	0.7445	0.340	0.760	6.0*
0.6148	2.068	0.831	0.6715	0.374	0.728	8.4†
0.9291	3.145	0.853	0.609	0.400	0.688	13.1†

NH<sub>4</sub>Cl.  $H = 3.3$ .  $K = 0.32$ .

0.005	0.01818	0.947	0.946	0.316	0.941	0.04
0.01	0.036	0.928	0.927	0.339	0.931	0.06
0.02	0.071	0.908	0.906	0.346	0.912	0.12
0.05	0.1744	0.880	0.874	0.342	0.881	0.30
0.1	0.344	0.856	0.845	0.334	0.850	0.60
0.2	0.6784	0.832	0.811	0.323	0.813	1.2
0.2619	0.889	0.835	0.801	0.313	0.795	1.55*
0.3	1.0086	0.819	0.783	0.324	0.786	1.8
0.7974	2.658	0.820	0.734	0.287	0.703	4.75*
1.0523	3.51	0.830	0.715	0.283	0.675	6.3*
2.32	7.72	0.863	0.611	0.294	0.576	13.9†
3.727	12.52	0.934	0.506	0.319	0.504	22.1†

RbCl.  $H = 2.9$ .  $K = 0.32$ .

0.1095	0.379	0.867	0.856	0.301	0.845	0.58*
0.2404	0.812	0.826	0.800	0.322	0.799	1.27*
0.4061	1.347	0.7985	0.7605	0.323	0.762	2.12*
0.5866	1.927	0.788	0.732	0.320	0.730	3.06*
0.7608	2.483	0.792	0.721	0.306	0.705	4.0*

CsCl.  $H = 2.7$ .  $K = 0.32$ .

0.02	0.0717	0.931	0.929	0.262	0.912	0.1
0.05	0.1757	0.893	0.889	0.301	0.881	0.25
0.1	0.3454	0.863	0.854	0.315	0.850	0.50
0.2	0.677	0.8285	0.810	0.325	0.811	1.0
0.3	1.002	0.808	0.780	0.327	0.784	1.5
0.4	1.322	0.792	0.755	0.332	0.762	2.0
0.5	1.637	0.778	0.734	0.340	0.744	2.5
0.693	2.24	0.761	0.6995	0.340	0.714	3.5*

Noyes and Falk's values, except those marked \* (Biltz), † (Ponsot), and ‡ (Radebush).



(compare  $\text{KNO}_3$  Adams with  $\text{CsNO}_3$  Washburn) and in the most dilute solutions agree better with the calculated value for chlorides ( $K = 0.32$ ) than for nitrates ( $K = 0.52$ ).

Table XIII refers to the four remaining univalent chlorides. With the exception of sodium chloride, they all obey the law in a satisfactory way, having a common value of  $K = 0.32$ . Sodium chloride deviates somewhat, the value of  $K$  increasing with concentration for solutions above  $0.25N$ . This is unexpected, since the viscosity is normal, and lithium chloride with its greater hydration number obeys the law, as does sodium bromide (Table XIV).

Table XIV gives a representative selection of the other salts investigated, viz., sodium bromide, magnesium chloride, barium chloride, and strontium nitrate, and it will be seen that in each

TABLE XIV.

NaBr. $H = 6.4$ . $K = 0.29$ .						
$n$ .	$\Delta t$ .	$\alpha$ .	$\alpha$ (corr.)	$K$ .	$\alpha$ (calc.)	%.
0.02	0.0722°	0.944	0.944	0.203	0.923	0.23†
0.05	0.1775	0.910	0.903	0.263	0.895	0.56†
0.1	0.3507	0.891	0.867	0.286	0.868	1.1†
0.2	0.6926	0.871	0.829	0.292	0.833	2.2†
0.3	1.031	0.860	0.798	0.301	0.809	3.4†
0.4872	1.691	0.886	0.783	0.276	0.772	5.4†
0.6434	2.232	0.890	0.755	0.284	0.750	7.2†
0.9731	3.413	0.923	0.707	0.296	0.713	10.9†
1.1632	4.112	0.946	0.694	0.291	0.695	13.0†
1.3544	4.820	0.965	0.670	0.291	0.671	15.1†
MgCl <sub>2</sub> . $H = 24.8$ . $K = 0.49$ .						
0.0562	0.282	0.852	0.818	0.475	0.812	2.60†
0.1180	0.580	0.827	0.757	0.495	0.760	5.3†
0.1665	0.822	0.834	0.735	0.482	0.730	7.45†
0.25072	1.235	0.835	0.682	0.504	0.691	11.5
0.5046	2.6768	0.999	0.622	0.475	0.610	22.5
0.76106	4.433	1.09	0.552	0.491	0.553	34.0
0.9608	6.062	1.34	0.503	0.504	0.517	43.0
BaCl <sub>2</sub> . $H = 16.2$ . $K = 0.55$ .						
0.05005	0.2477	0.833	0.817	0.497	0.797	1.46
0.07514	0.3613	0.796	0.762	0.564	0.768	2.2
0.1003	0.4792	0.789	0.751	0.536	0.745	2.8
0.16312	0.757	0.754	0.695	0.558	0.699	4.75§
0.1727	0.804	0.753	0.694	0.550	0.694	5.05§
0.4043	1.902	0.779	0.628	0.502	0.593	11.8
1.205*	7.85	1.33	0.443	0.524	0.415	35.5
Sr(NO <sub>3</sub> ) <sub>2</sub> . $H = 6.8$ . $K = 0.58$ .						
0.1004	0.4587	0.733	0.718	0.607	0.730	1.2
0.2528	1.0817	0.655	0.620	0.601	0.634	3.1
0.5116	2.0849	0.609	0.541	0.574	0.537	6.15
0.7771	3.0453	0.574	0.472	0.570	0.467	9.4
1.0506	3.9983	0.544	0.411	0.579	0.411	12.7
1.530*	5.75	0.543	0.352	0.562	0.332	18.4

Jones's values, except those marked † (Noyes and Falk), ‡ (Rivett), § (Ponsot), and || (de Coppet).

\* Cryohydric concentration.

case the cube root law is obeyed and applies equally well to bi-univalent salts of the type  $\text{BaCl}_2$ ,  $\text{Sr}(\text{NO}_3)_2$ , etc.

In addition to the above salts, calculations have been made for a number of others with the following results: sodium nitrate ( $K = 0.38$ ), potassium nitrate ( $K = 0.50$ ), and rubidium nitrate ( $K = 0.51$ ) obey the cube root law, with the possible deviation of potassium nitrate in dilute solution (see Table XII and comments). The small value of  $K$  for sodium nitrate should be noted. Potassium bromide gave less satisfactory results,  $K$  decreasing from 0.31 for dilute solutions to 0.24 at the eutectic (3.836-weight normal). This salt behaves as if the hydration value of 1.9 is too small; the experimental result, however, is beyond suspicion. An increase of  $H$  by one unit (which is not justified on any other grounds) would give a constant value of  $K$  at all concentrations.

Calcium chloride ( $K = 0.47$ ), strontium chloride ( $K = 0.48$ ), cobalt chloride ( $K = 0.45$ ), and copper chloride ( $K = 0.52$ ) are all satisfactory. With barium nitrate ( $K = 0.80$ ), the constant tends to rise slightly, and with lead nitrate ( $K = 0.93$ ) to fall slightly, both in dilute solution; but this is thought to be due to possible small errors in the freezing-point measurements. Copper bromide gives a small but constant value ( $K = 0.31$ ), whilst barium bromide resembles the potassium salt, the values of  $K$  decreasing from 0.44 to 0.36.

Thus far, the results for twenty-two salts have either been given in detail or commented upon, and considerable evidence has been adduced in favour of the cube root law. In only three of the above cases do deviations occur, *viz.*, sodium chloride and potassium and barium bromides, but five other salts were found not to obey the law. These are the nitrates of lithium, magnesium, calcium, copper, and cobalt, for which  $K$  decreases continuously with increasing concentration: *e.g.*, magnesium nitrate  $n = 0.05$ ,  $K = 0.46$ ;  $n = 1.0423$ ,  $K = 0.13$ ; calcium nitrate  $n = 0.05$ ,  $K = 0.58$ ;  $n = 1.05$ ,  $K = 0.42$ ; lithium nitrate  $n = 0.04$ ,  $K = 0.52$ ;  $n = 1.016$ ,  $K = 0.24$ . These salts all contain heavily hydrated cations, and anions which are very active in dissociating the solvent. Although the hydration numbers of these salts are relatively small, since they represent the *difference* between two competing processes, they do not afford a measure of the great disturbance suffered in these cases by the solution.

The apparent molecular hydration of magnesium nitrate is  $12.8 \text{ H}_2\text{O}$ ; in a molar solution of this salt, not less than half the solvent is attached to the magnesium ions and the activity of the remainder is increased by 50% by the nitrate ions. It is doubtful, therefore, whether the use of a *constant* hydration correction is

permissible, even if Washburn's equation is applicable to cases where the solvent equilibrium is so violently disturbed. Where the absolute hydration correction is small (potassium chloride) the cube root law is followed with great exactness, even for dilute solutions, and it appears probable that an ideal strong electrolyte (anion inert, kation not hydrated) would obey the law over the whole concentration range.

*The Hydration Theory and the Conductivity Ratio.*

According to the theory of complete dissociation, the conductivity ratio  $\lambda_v/\lambda_{\infty}$  must be regarded solely as a ratio of mobilities, the mobility of the ions decreasing as the concentration increases, and this decrease is probably to a large degree due to the decreasing distance between the charged ions. If no other influence intervened, it is to be expected that the conductivity ratio would depend only on the type of salt and be independent of the ion carrying the charge. We know, however, that the so-called "dissociating power" of a solvent depends on the magnitude of its dielectric constant, whilst the latter is related to the molecular association of the solvent. The hydration theory suggested in this paper postulates a continuous decrease in the association of the solvent, and consequently a decrease in the dielectric constant, with increasing salt concentration, whilst the efficiency of the depolymerisation process varies with different anions. The conductivity ratio, therefore, should not only decrease as the concentration of salt increases, but it should do so at rates which depend on the sequence of the hydration numbers (see p. 186). For the potassium salts at semi-normal concentration at 18°, the order of the conductivity ratios is that required by the hypothesis, viz., KCl, 0.779; KBr, 0.766; KClO<sub>3</sub>, 0.703; KNO<sub>3</sub>, 0.688.

EXPERIMENTAL.

The amyl alcohol was washed with dilute sulphuric acid and with water, dried over potassium carbonate, and distilled, the fraction boiling at 128—132° being collected. The distribution coefficients were determined by shaking together 100 c.c. of the alcohol, 100 c.c. of the solution to be examined, and 1 c.c. of purified acetic acid at 25° until equilibrium was established. After the two phases had separated completely, the alcoholic layer was drawn off rapidly and the acid content determined by titration with N/20-barium hydroxide and phenolphthalein. Owing to the different nature of the two solvents it was found advisable to wash out the pipette with either 20 c.c. of water or 20 c.c. of purified ethyl alcohol, according as the aqueous or non-aqueous

phase was being examined. In the latter case, the ethyl alcohol brought the amyl alcohol into complete solution and so facilitated the titration. It was necessary to carry out blank experiments on each batch of amyl alcohol, owing to slight variations of the coefficient with different samples (presumably due to differences in the proportion of the isomerides present). The average value of the coefficient alcohol to water was 0.96.

The viscosity measurements were carried out in an Ostwald viscosimeter at 20°, and whilst no outstanding accuracy is claimed for these results, all ordinary precautions were observed.

### *Summary.*

The hydration of sucrose and some strong electrolytes has been determined from the distribution of acetic acid between their aqueous solutions and amyl alcohol. The results indicate that the hydration is (over the concentration range examined) independent of dilution and is an additive property which may have either a positive or a negative value.

A modified hydration theory is suggested according to which only kations are hydrated whilst anions depolymerise the solvent molecules. The first process tends to decrease and the second to increase the activity of the water. Hydration is therefore a composite effect, the salts having negative hydration numbers being those in which the influence of the anion predominates. Solutions of such salts have abnormally high vapour pressures.

The hydration theory has been correlated with viscosity phenomena and a semi-empirical equation established by means of which hydration values can be calculated from viscosity data.

A hydration correction has been applied to calculations of the "degree of dissociation" of strong electrolytes from freezing-point measurements, and evidence is adduced in favour of a cube root dilution law  $(1 - \alpha) = K\sqrt[3]{n}$ . Many salts have been shown to obey the law with great exactness, and those which do not do so are extreme cases in which the application of the correction is least certain.

Corroborative evidence for the new theory has been obtained from a consideration of the conductivity ratios of a number of strong electrolytes.

The author wishes to thank Messrs. Brunner Mond & Co. for a grant from their research fund which defrayed part of the cost of the investigation.

XXIX.—*Action of Acetylene Tetrabromide on Organic Bases.*

By JAMES DAVIDSON FULTON.

THE present investigation, in which the reagents were allowed to react in the absence of a solvent, was suggested by the action of nicotine on acetylene tetrabromide. The rotation of the solution changed rapidly from negative to positive and the solution became hot and coloured; after a few days a solid separated, whilst some oily matter remained. The latter, usually small in amount, was discarded in this and subsequent experiments.

The interaction of aniline and acetylene tetrabromide at the ordinary temperature was investigated by Sabanejev (*Annalen*, 1875, 178, 125), who obtained a number of products including acetylenetriphenyltriamine,  $C_{20}H_{17}N_3$ . Schoop (*Ber.*, 1880, 13, 2196) obtained octamethyltetra-aminotetraphenylethane by heating dimethylaniline with acetylene tetrabromide for 8 days. Elbs and Neumann (*J. pr. Chem.*, 1898, 58, 250) failed to substantiate all the findings of Sabanejev. In the above cases, the hydrobromide of the base also was obtained. Dehn (*J. Amer. Chem. Soc.*, 1912, 34, 286) has shown that the reaction of bases and acetylene tetrabromide in dry ether furnishes the hydrobromide and tribromoethylene quantitatively and that sunlight accelerates the reaction.

In the present instance, in the case of tertiary bases additive compounds of the hydrobromide with acetylene tetrabromide were obtained. The influence of sunlight on their formation was not marked. Abnormal bromoaurates were obtained from nicotine and quinoline.

## EXPERIMENTAL.

Acetylene tetrabromide (usually 2 or 3 mols.) was added to the base (1 mol.) in the cold. Solid hydrobromides were immediately precipitated from primary and secondary amines. With tertiary bases, a solid separated after a day or two. In the case of  $\alpha$ -picoline, although reaction was apparent, no crystals appeared for weeks until the mixture was cooled in liquid air and again left. The solid product was filtered off, freed from oily matter, and crystallised from alcohol. The well-crystallised substances thus obtained were all soluble in cold methyl or ethyl alcohol and very soluble in the hot solvent; repeated crystallisation brought about a partial change to the hydrobromide. A single crystallisation from acetone or chloroform effects this change almost completely. The compounds are slightly or not at all soluble in other common organic solvents. The total bromine and the ionisable bromine were estimated.

Water decomposes these compounds. Acetylene tetrabromide is liberated, and the supernatant aqueous solution contains the hydrobromide of the base, which was recognised, in the case of pyridine and quinoline, by analysis and melting point.

The bromoaurates separated when hot alcoholic solutions of the additive compounds, to which auric bromide in alcohol had been added, were allowed to cool.

*Nicotine*:  $C_{10}H_{14}N_2 \cdot 2HBr \cdot 2C_2H_2Br_4$ , needles, or rhombs by slow crystallisation, m. p. 178—180° (decomp.), softening at 140° (Found: total Br, 79.0; Br', 15.9. Calc., 78.7 and 15.7%, respectively).  $[\alpha]_{D}^{25} + 3.21^\circ$  in alcohol ( $c = 5.6025$ ).

The bromoaurate,  $C_{10}H_{14}N_2 \cdot 2HBr \cdot AuBr_3$ , forms dark red crystals, m. p. 183°, which are soluble in alcohol and slightly soluble in water (Found: Au, 26.05. Calc., Au, 25.9%).

A more stable, less soluble compound,  $[\alpha]_{D}^{25} + 6.96^\circ$  in alcohol ( $c = 5.6025$ ), m. p. 182—183° (decomp.), giving the same bromoaurate (Found: Au, 26.0%), was obtained by repeated crystallisation of the above and also from 1 mol. of the base and 1 mol. of acetylene tetrabromide [Found: total Br, 64.4; Br', 32.3. ( $C_{10}H_{14}N_2 \cdot 2HBr$ ) $_2 \cdot C_2H_2Br_4$  requires Br, 64.4; Br', 32.2%].

*Pyridine*:  $C_5H_5N \cdot HBr \cdot C_2H_2Br_4$ , colourless crystals, m. p. 108—109° (Found: total Br, 79.15; Br', 16.05. Calc., Br, 79.05; Br', 15.8%).

The bromoaurate forms brownish-red crystals, m. p. 318—319° (Found: Au, 33.0.  $C_5H_5N \cdot HBr \cdot AuBr_3$  requires Au, 33.0%).

*Quinoline*: The product was washed with a little alcohol and ether. It softened at 115° and melted at 136° [Found: total Br, 62.4; Br', 21.2. ( $C_9H_7N \cdot HBr$ ) $_2 \cdot C_2H_2Br_4$  requires Br, 62.7; Br', 20.9%]. This substance is analogous to the lead compound, ( $C_9H_7N \cdot HBr$ ) $_2 \cdot PbBr_4$  (Classen and Zahorski, *Z. angew. Chem.*, 1891, 4, 107).

The bromoaurate forms dark red crystals, m. p. 171—172°, which are soluble in alcohol and slightly soluble in water [Found: Au, 23.0. ( $C_9H_7N \cdot HBr$ ) $_2 \cdot AuBr_3$  requires Au, 23.0%]. It is analogous to Fenner and Tafel's chloro-compound (*Ber.*, 1899, 32, 3227).

isoQuinoline gave mostly its hydrobromide, m. p. 207° (Found: Br, 38.0. Calc., Br, 38.1%). The additive compound, m. p. 155—156°, was almost colourless and not quite pure [Found: total Br, 61.4; Br', 22.5. ( $C_9H_7N \cdot HBr$ ) $_2 \cdot C_2H_2Br_4$  requires Br, 62.7; Br', 20.9%].

The bromoaurate, obtained from the hydrobromide in dark red crystals, m. p. 223°, was normal (Found: Au, 30.25. Calc. for  $C_9H_7N \cdot HBr \cdot AuBr_3$ , Au, 30.5%).

*Lucidine*, b. p. 153—156° (regarded as 2:4-dimethylpyridine):

Colourless crystals, m. p. 135—140° [Found: total Br, 66·7; Br', 22·3.  $(C_7H_9N, HBr)_2, C_2H_2Br_4$  requires Br, 66·5; Br', 22·2%].

$\alpha$ -Picoline:  $C_6H_7N, HBr, C_2H_2Br_4$ , colourless needles, m. p. 104—105° (Found: total Br, 76·8; Br', 15·4. Calc., Br, 76·9; Br', 15·4%).

Interaction of acetylene tetrabromide and piperidine, coniine, homopiperonylamine, menthylamine, hexamethylenetetramine, and phenylhydrazine gave rise to the hydrobromide only. Antipyrine dissolved in hot acetylene tetrabromide crystallised unchanged on cooling. Pyrrole also did not react.

I desire to thank Professor T. S. Patterson for his interest in this work and for facilities to carry it out.

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[Received, October 2nd, 1925.]

### XXX.—*Heterogeneous Equilibria between the Sulphates and Nitrates of Sodium and Potassium and their Aqueous Solutions. Part I. The Ternary Systems.*

By MOHAMMED ABDUL HAMID.

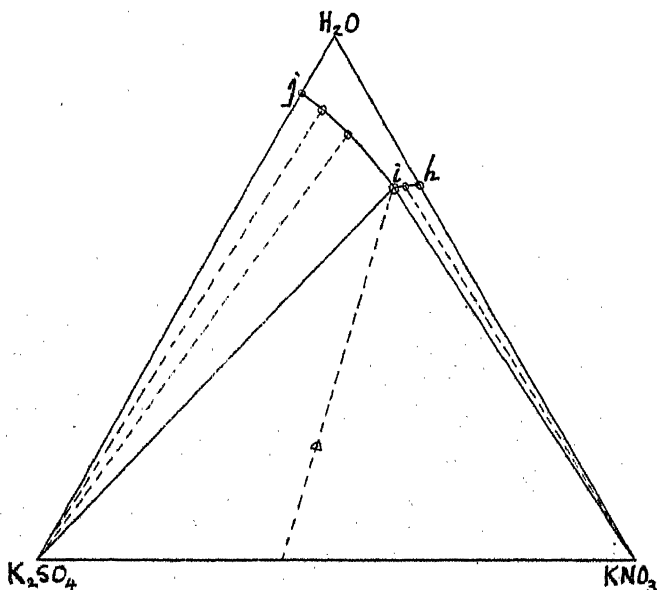
DURING the course of an investigation of the quaternary system  $H_2O-Na_2SO_4-NaNO_3-K_2SO_4-KNO_3$  at 25° and 90°, it became necessary to investigate and revise some of the ternary systems involved. The subject of the present paper is to record the data so obtained and to sum up briefly all other information available about the isothermal relations in the four ternary systems which form the basis of the above quaternary system. In the isotherms at 90°, only the invariant points have been determined. The solubilities of single salts have been selected from Seidell's "Solubilities of Inorganic and Organic Substances." The vapour phase is always assumed to be absent and the whole subject is treated from the point of view of condensed systems at atmospheric pressure.

#### EXPERIMENTAL.

All the salts used were carefully purified by repeated crystallisation and their purity was checked by a number of analyses before use. For the determination of solubility, various complexes were vigorously stirred up to equilibrium in wide tubes immersed in water- and oil-thermostats kept constant within 0·02° at 25° and within 0·2° at 90°. The usual time given was about 40 hours at 25° and about 10 hours at 90°. The compositions of the solutions when equilibrium was established were determined by withdrawing

portions of them by means of pipettes heated previously to the temperatures of the baths, filtering, and weighing in stoppered bottles and analysing the solutions. The moist residue was weighed separately and analysed. The potassium ion was determined by the cobaltinitrite method, sulphate weighed as barium sulphate, and nitrate estimated by a modified method of Schlösing. All these methods were checked beforehand by a large number of estimations in mixtures of sodium sulphate, sodium nitrate, potassium sulphate, and potassium nitrate of known compositions. The amounts of sodium and water were determined by difference. In

FIG. 1.



some cases all the salts were converted into the chlorides and the analytical results checked in this way.

The thermometers were all compared with those standardised at the National Physical Laboratory, Teddington.

*The System Water-Potassium Sulphate-Potassium Nitrate.*—This belongs to the simplest type of ternary system, neither double salts nor salt hydrates occurring in it. The system at 25° is represented graphically in Fig. 1, and the experimental data for the two temperatures are in Table I.

The system water-sodium nitrate-potassium nitrate has been worked out by Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1935) at 25°. The compositions of the binary and ternary invariant solutions at 90° are in Table II.



TABLE I.

Composition by weight percentage.

Temp.	Solution.		Rest.		Solid phases.
	% $K_2SO_4$ .	% $KNO_3$ .	% $K_2SO_4$ .	% $KNO_3$ .	
25°	10.74	0	—	—	$K_2SO_4$
"	8.85	4.82	—	—	"
"	6.89	11.05	—	—	"
"	4.45	23.99	43.18	36.75	$K_2SO_4 + KNO_3$
"	1.98	26.01	—	—	$KNO_3$
"	0	27.97	—	—	"
90°	18.57	0	—	—	$K_2SO_4$
"	0.63	65.92	—	—	$K_2SO_4 + KNO_3$
"	0	66.90	—	—	$KNO_3$

TABLE II.

Composition by weight percentage.

% $NaNO_3$ .	% $KNO_3$ .	Solid phases.
61.65	0	$NaNO_3$
37.57	45.26	$NaNO_3 + KNO_3$
0	66.90	$KNO_3$

The system water-potassium sulphate-sodium sulphate is complicated by the existence of a double sulphate of sodium and potassium known as the mineral glaserite. As to the composition of this compound, there have been controversies from time to time. Its correct composition was first reported by Penny (*Phil. Mag.*, 1855, 10, 401), who assigned the formula  $3K_2SO_4 \cdot Na_2SO_4$  to it and after whom it is sometimes called Penny's double salt. Penny's results were corroborated by some authors, whilst several double sulphates of sodium and potassium of different compositions were subsequently described by various investigators. A complete literature on this subject can be found in a paper by Retgers (*Z. physikal. Chem.*, 1890, 6, 205). van 't Hoff and Barschall (*Berlin. Sitzungsber.*, 1903, 359; *Z. physikal. Chem.*, 1906, 56, 212) put forward the view that glaserite is an extreme limit of a series of solid solutions saturated with potassium sulphate having the composition  $K_3Na(SO_4)_2$ . Nacken (*Berlin. Sitzungsber.*, 1910, 1016) has confirmed the existence of the double salt  $K_3Na(SO_4)_2$  and has found that it dissolves sodium sulphate as a solid solution up to a certain extent. His results have been confirmed recently by Okada (*Mem. Coll. Sci.*, 1914, 1, 95). Whereas Nacken assumes that the solubility of sodium sulphate in glaserite increases with temperature, Okada has shown that it increases to a temperature of 60°, where it reaches a maximum, and above that temperature the field of solid solutions becomes narrower again. The system  $H_2O-K_2SO_4-Na_2SO_4$  at 25° and 90° is shown in Figs. 2 and 3

respectively. The data for this system at these two temperatures are in Table III.

TABLE III.

Composition by weight percentage.

Temp.	% $\text{Na}_2\text{SO}_4$ .	% $\text{K}_2\text{SO}_4$ .	Solid phases.
25°	21.84	0	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
"	19.93*	7.06	$\{\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{mixed crystals of}$
"	5.58*	11.27	$\text{K}_2\text{Na}(\text{SO}_4)_2 \text{ and } \text{Na}_2\text{SO}_4$
"	0	10.74	$\text{K}_2\text{SO}_4 + \text{K}_2\text{Na}(\text{SO}_4)_2$
90°	29.90	0	$\text{Na}_2\text{SO}_4$
"	27.05	8.33	$\{\text{Na}_2\text{SO}_4 + \text{mixed crystals of } \text{Na}_2\text{SO}_4$
"	9.23	14.97	$\text{and } \text{K}_2\text{Na}(\text{SO}_4)_2$
"	0	18.57	$\text{K}_2\text{SO}_4 + \text{K}_2\text{Na}(\text{SO}_4)_2$
"			$\text{K}_2\text{SO}_4$

\* Meyerhoffer and Saunders, *Z. physikal. Chem.*, 1899, 28, 482.

FIG. 2.

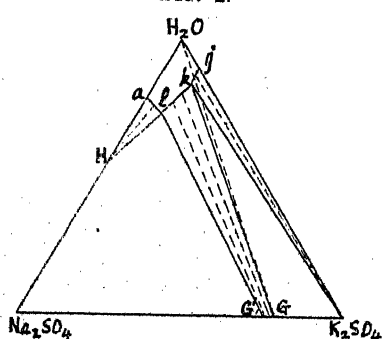
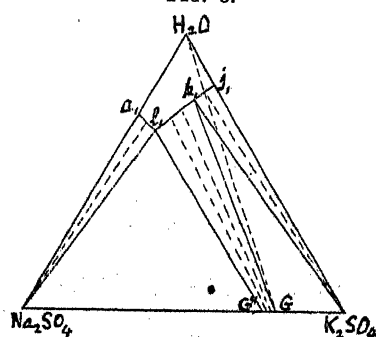


FIG. 3.



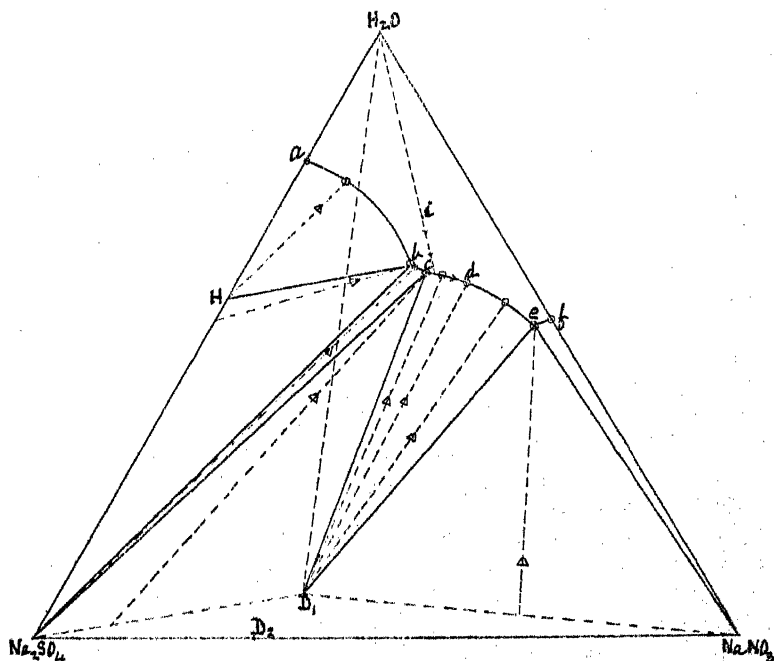
The points H and G (Figs. 2 and 3) represent the compositions of pure Glauber's salt and pure glaserite, respectively. The point G' (Fig. 2) represents the composition of the solid solution containing the maximum amount of sodium sulphate which glaserite can dissolve at 25°. Similarly the point G'' (Fig. 3) represents the composition of the solid solution which is formed by dissolving the maximum amount of sodium sulphate in glaserite at 90°. The compositions of G, G', and G'' are given in Table IV, both in terms of weight (*w*) and molar (*m*) percentages.

TABLE IV.

Temp. 25° :	Comp. of G.		Comp. of G'.		Diff.
	$\text{K}_2\text{SO}_4$ .	$\text{Na}_2\text{SO}_4$ .	$\text{K}_2\text{SO}_4$ .	$\text{Na}_2\text{SO}_4$ .	
<i>m</i> .....	75.0	25.0	71.7	28.3	3.3
<i>w</i> .....	78.6	21.4	75.7	24.3	2.9
Temp. 90° :	Comp. of G.		Comp. of G''.		Diff.
	$\text{K}_2\text{SO}_4$ .	$\text{Na}_2\text{SO}_4$ .	$\text{K}_2\text{SO}_4$ .	$\text{Na}_2\text{SO}_4$ .	
.....	75.0	25.0	70.5	29.5	4.5
.....	78.6	21.4	74.6	25.4	4.0

The above values of  $G'$  are taken from Nacken and Okada and those of  $G''$  interpolated from Okada's results. It will be seen from the isotherms at  $25^\circ$  and  $90^\circ$  (Figs. 2 and 3) that the solutions  $l$  and  $l_1$  are in equilibrium with Glauber's salt and  $G'$  in one case, and with sodium sulphate and  $G''$  in the other. The solutions all along the curves  $lk$  and  $l_1k_1$  are in equilibrium with solid solutions whose compositions vary between  $G$  and  $G'$  in one case and between  $G$  and  $G''$  in the other. It may be mentioned that glaserite is not known to form any solid solutions with potassium sulphate.

FIG. 4.



*The System Water-Sodium Sulphate-Sodium Nitrate.*—This system has been very recently worked out by Massink (*Z. physikal. Chem.*, 1917, 92, 364) at a number of temperatures. In addition to a hydrated double salt of the formula  $\text{Na}_2\text{SO}_4 \cdot \text{NaNO}_3 \cdot \text{H}_2\text{O}$ , commonly known in Chile as the mineral darapskite, Massink describes an anhydrous double salt of the formula  $3\text{NaNO}_3 \cdot 4\text{Na}_2\text{SO}_4$  at  $25^\circ$ . No evidence of this double salt could be obtained at this temperature. The only double salt that exists at  $25^\circ$  is the hydrated double salt, darapskite, which breaks up at higher temperatures, and at  $90^\circ$  the only stable solid phases in the system are the two anhydrous

salts, sodium sulphate and sodium nitrate. The system at 25° is shown in Fig. 4, and the data for this system at the two temperatures are in Table V.

TABLE V.

Composition by weight percentage.

Solution.			Rest.		
Temp.	% $\text{Na}_2\text{SO}_4$ .	% $\text{NaNO}_3$ .	% $\text{Na}_2\text{SO}_4$ .	% $\text{NaNO}_3$ .	Solid phases.
25°	21.84	0	—	—	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
"	17.52	7.48	23.37	6.15	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}$
"	15.70	23.43	24.82	16.58	
"	15.43	24.06	34.43	18.40	$\text{Na}_2\text{SO}_4$
"	14.15	25.96	39.87	20.45	$\text{Na}_2\text{SO}_4 + \text{D}_1$
"	11.88	28.46	30.00	31.05	$\text{D}_1$
"	9.04	32.68	27.44	33.46	"
"	5.42	39.71	29.39	37.52	"
"	3.01	45.87	24.63	62.90	$\text{D}_1 + \text{NaNO}_3$
"	0	47.69	—	—	$\text{NaNO}_3$
90°	29.90	0	—	—	$\text{Na}_2\text{SO}_4$
"	2.53	58.66	—	—	$\text{Na}_2\text{SO}_4 + \text{NaNO}_3$
"	61.65	0	—	—	$\text{NaNO}_3$

Composition of  $\text{D}_1 = \text{Na}_2\text{SO}_4$ , 57.96%;  $\text{NaNO}_3$ , 34.68%;  $\text{H}_2\text{O}$ , 7.36%.

The points H and  $\text{D}_1$  (Fig. 4) represent the compositions of pure Glauber's salt and pure darapskite, respectively. The point  $\text{D}_2$  (Fig. 4) represents the composition of the supposed anhydrous double salt of Massink and the point  $d$  his supposed ternary isothermal invariant point at which, according to him, the solution is in equilibrium with darapskite and the anhydrous double salt  $\text{D}_2$ . Not only has this solution been found to be saturated with darapskite alone, but on isothermal evaporation of unsaturated solutions at 25° which theoretically ought to have deposited the anhydrous double salt  $\text{D}_2$ , if it could exist, darapskite has been found to be precipitated as the first solid. Thus an unsaturated solution of the composition  $i$  (Fig. 4) on evaporation at 25°, according to Massink, should deposit the anhydrous double salt  $\text{D}_2$  as the first solid and should continue to do so until the point  $d$  is reached. This it does not do. Instead, however, it deposits darapskite, which comes down in very fine, needle-shaped crystals, readily distinguishable with the naked eye. Besides the double salt  $\text{D}_2$ , Massink (*loc. cit.*) describes another anhydrous double salt of the formula  $3\text{NaNO}_3 \cdot 2\text{Na}_2\text{SO}_4$  at 35°. It may be noted that he has determined the compositions of these two anhydrous double salts from one or two analyses of the solution and the wet residue in each case, which in themselves are not sufficient. The improbability of the existence of these two anhydrous double salts in this system is further manifest from the following considerations. It has been

alleged by Massink himself that these two anhydrous double salts do not exist at lower temperatures. According to him, the transition temperatures which mark the lower stability limits to the existence of the two anhydrous double salts lie somewhere between  $20^{\circ}$  and  $35^{\circ}$ . Further, it has been shown by Schreinemakers (*Z. physikal. Chem.*, 1909, **65**, 553) that if two anhydrous salts can form an anhydrous double salt at a certain temperature in the binary system, formed by these two salts, they will do so at the same temperature in all ternary systems formed by the addition of any liquid component to the above binary system, and the solubility curves of the two salts will be interrupted by that of the double salt in all these systems at this temperature. The converse of this principle has been very recently applied by Freeth (*J. Physical Chem.*, 1925, **29**, 1497) in the deduction of the type of a two-component system by the addition of a third component, from which it follows that if above a certain temperature in the ternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$  the solubility curves of sodium sulphate and sodium nitrate are interrupted by that of an anhydrous double salt, this will be the case also in the binary system  $\text{Na}_2\text{SO}_4-\text{NaNO}_3$ . Since the solution does not participate in the formation of the anhydrous double salt, the transition temperature of this binary compound is independent of the number of components of the system, *i.e.*, it is the same in all systems whether binary, ternary, or quaternary. It is clear, therefore, that at temperatures above  $35^{\circ}$  the two anhydrous double salts of Massink, if they can exist at all, must be formed in the ternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$ , as also in the binary system  $\text{Na}_2\text{SO}_4-\text{NaNO}_3$ . From an investigation of the quaternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{K}_2\text{SO}_4-\text{KNO}_3$  at  $90^{\circ}$  the author has been led to the conclusion that no such double salts exist in the ternary system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$  at this temperature, the only solid phases being the two anhydrous salts, sodium sulphate and sodium nitrate. This is in complete accord with the very recent investigations of Perman and Harrison (*J.*, 1924, **125**, 365) of the binary system  $\text{Na}_2\text{SO}_4-\text{NaNO}_3$ .

The author wishes to express his thanks to Professor F. G. Donnan, F.R.S., for his kind help and interest during the course of this investigation.

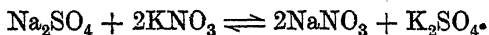
THE WILLIAM RAMSAY INORGANIC AND  
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UNIVERSITY COLLEGE, LONDON. [Received, December 1st, 1925.]

XXXI.—*Heterogeneous Equilibria between the Sulphates and Nitrates of Sodium and Potassium and their Aqueous Solutions. Part II. The Quaternary System  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{K}_2\text{SO}_4-\text{KNO}_3$ .*

By MOHAMMED ABDUL HAMID.

BEYOND the observations of some early investigators of the slow dissolution of potassium nitrate in saturated sodium sulphate solutions with the precipitation of sodium or potassium sulphate after a long time and of the ease with which sodium nitrate dissolves in solutions of potassium sulphate, no attempt seems ever to have been made to study the equilibria involved in the reciprocal salt transformation



The quaternary system formed by the addition of water to the two salt pairs,  $\text{Na}_2\text{SO}_4-\text{KNO}_3$  and  $\text{NaNO}_3-\text{K}_2\text{SO}_4$  presents certain features of interest and is of special importance in the determination of the most suitable conditions for the separation of the nitrates of sodium and potassium from the sulphates of these metals, with which they are found contaminated in nature in various parts of the world.\*

The various binary and ternary systems which form the basis of the above quaternary system have been described in Part I (preceding paper). All the binary and ternary compounds which occur in the ternary systems occupy definite saturation surfaces in the quaternary system. In addition to these binary and ternary compounds at  $25^\circ$ , a compound occurs in the quaternary system, the composition of which it has not been found possible so far to determine. It occupies a definite saturation surface in the quaternary system, and further evidence on which the conclusion of its existence is based will be found in the following pages. The isotherm at  $90^\circ$  does not contain the saturation surface of this compound. There is therefore no doubt that it splits up at some temperature below  $90^\circ$  into its simple constituents.

*Graphical Representation.*—In order to represent graphically the experimental results, Schreinemaker's pyramidal method of representation (*Z. physikal. Chem.*, 1909, 69, 557) has been used. Use has also been made of the various projection methods (*ibid.*, 1907,

\* See "Report on a Programme of Investigation for the Chilean Nitrate Industry," 1921, by Professor F. G. Donnan; the Report of the Indian Industrial Commission, 1916-18, Appendix F; and a Report on the Manufacture and Composition of Indian Saltpetre by Hooper (*Agricultural Ledger*, No. 3, 1905).

TABLE I.

*The System*  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{K}_2\text{SO}_4-\text{KNO}_3$  at 25°.

Composition in molar percentages.

Point.	$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2(\text{NO}_3)_2$ .	$\text{K}_2\text{SO}_4$ .	$\text{K}_2(\text{NO}_3)_2$ .	Solid phases.
<i>a</i>	3.42	—	—	—	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$
	2.85	1.02	—	—	
<i>b</i>	3.05	3.80	—	—	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
<i>l</i>	3.35	—	0.96	—	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} + \text{D}_2$
<i>m</i>	2.89	2.75	0.74	—	$\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 + \text{D}_2$
	3.01	3.92	—	—	$\text{Na}_2\text{SO}_4$
<i>c</i>	2.78	4.27	—	—	$\text{Na}_2\text{SO}_4 + \text{D}_1$
	2.76	4.44	0.67	—	
<i>n</i>	2.66	4.49	1.27	—	$\text{Na}_2\text{SO}_4 + \text{D}_1 + \text{D}_2$
	2.34	4.70	—	—	$\text{D}_1$
	1.82	5.51	—	—	"
	1.15	7.04	—	—	"
<i>e</i>	0.68	8.83	—	—	$\text{D}_1 + \text{NaNO}_3$
	0.74	8.47	—	0.23	
<i>r</i>	1.05	7.91	—	0.60	$\text{D}_1 + \text{NaNO}_3 + \text{T}$
<i>f</i>	—	8.81	—	—	$\text{NaNO}_3$
	—	8.97	—	0.40	"
	—	9.03	—	0.80	"
	—	9.10	—	1.59	"
	—	9.18	—	2.36	"
<i>g</i>	—	9.31	—	3.58	$\text{NaNO}_3 + \text{KNO}_3$
	1.17	8.36	—	1.69	$\text{NaNO}_3 + \text{T}$
	0.77	8.97	—	3.20	
<i>s</i>	0.67	9.10	—	3.63	$\text{NaNO}_3 + \text{KNO}_3 + \text{T}$
	—	5.78	—	3.39	$\text{KNO}_3$
	—	3.94	—	3.26	"
	—	2.01	—	3.17	"
	—	1.52	—	3.18	"
	—	1.02	—	3.20	"
	—	0.51	—	3.26	"
<i>h</i>	—	—	—	3.34	"
	—	—	0.28	3.11	"
<i>i</i>	—	—	0.62	2.89	$\text{KNO}_3 + \text{K}_2\text{SO}_4$
	—	—	0.85	1.18	$\text{K}_2\text{SO}_4$
	—	—	1.04	0.49	"
<i>j</i>	—	—	1.23	—	"
<i>k</i>	0.83	—	1.34	—	$\text{K}_2\text{SO}_4 + \text{D}_2$
	1.18	—	1.09	0.44	"
	1.09	—	0.89	0.69	"
	0.99	—	0.32	1.75	"
<i>v</i>	—	1.16	0.92	2.70	$\text{K}_2\text{SO}_4 + \text{D}_2 + \text{KNO}_3$
	—	2.12	0.99	2.32	$\text{D}_2 + \text{KNO}_3$
	—	4.91	1.33	1.82	"
<i>q</i>	—	7.91	1.61	1.65	$\text{D}_2 + \text{KNO}_3 + \text{T}$
	—	8.47	0.96	2.32	$\text{KNO}_3 + \text{T}$
	1.63	5.42	1.60	—	$\text{D}_1 + \text{D}_2$
	1.08	6.35	1.92	—	"
	0.75	7.13	2.09	—	"
	0.13	8.32	2.30	—	"
<i>p</i>	—	9.13	2.27	0.41	$\text{D}_1 + \text{D}_2 + \text{T}$
	—	8.82	1.90	0.84	$\text{D}_2 + \text{T}$

 $\text{D}_1 = \text{Na}_2\text{SO}_4, \text{NaNO}_3, \text{H}_2\text{O}$ .  $\text{D}_2 = \text{K}_2\text{Na}(\text{SO}_4)_2$ .  $\text{T} = ?$ .

59, 663) for the confirmation of solid phases by the "rest method" in certain parts of the system. It may be pointed out that by the term, orthogonal projection, is meant a projection made on to the

ground plane by means of parallel lines perpendicular to the base of the pyramid.

The experimental and analytical methods used were the same as described in Part I. The data for the system  $\text{H}_2\text{O}-\text{NaNO}_3-\text{KNO}_3$  at  $25^\circ$  are taken from Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 16, 106).

*The Isotherm at  $25^\circ$ .*—The compositions of the binary, ternary and quaternary solutions saturated at this temperature are expressed in g.-mols. of the various salts per 100 g. of the solution in Table I. The molecular formulæ of sodium and potassium nitrates have been doubled in order to give them equal replacing powers with sodium and potassium sulphates.

*The Orthogonal Projection.*—For the further discussion of the system, we shall use the orthogonal projection which is shown in Figs. 1 and 2. The apex, W, of the pyramid which represents pure water projects to the point *w* in these figures. The four ternary isotherms which form the boundary of the quaternary isotherm are shown in this projection separately in Fig. 1. As has been pointed out in Part I, the point *l* represents a ternary isothermal invariant solution which is in equilibrium not with Glauber's salt and glaserite, but with Glauber's salt and a solid solution of glaserite and sodium sulphate of the composition  $\text{K}_2\text{SO}_4 = 78.6\%$ ,  $\text{Na}_2\text{SO}_4 = 21.4\%$ . This introduces no new complication in the quaternary system provided there is always an excess of sodium sulphate present in the solid phase to form the solid solution of glaserite and sodium sulphate of the above composition. Strictly speaking, therefore, where glaserite is mentioned as a solid phase along with sodium sulphate, its composition is given by the above value. The difference between the composition of glaserite and that of its solid solution is not, however, very large and for all practical purposes glaserite may be assumed to be of the constant composition  $\text{K}_3\text{Na}(\text{SO}_4)_2$ . It may be seen that the line joining the point representing the composition of pure glaserite to the origin (apex in the space model) cuts the saturation curve of potassium sulphate and not that of glaserite. Glaserite is therefore decomposed by water and the ternary invariant solution *l* is incongruently saturated.

In order to show the positions of the quaternary saturation surfaces of Glauber's salt and sodium sulphate and the quaternary isothermal invariant point *m* more clearly in the projection, the ternary saturation curve *ab* of Glauber's salt in the system  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3$  is drawn as a straight line in Fig. 2, although the actual form of the curve is that shown in Fig. 1.

The darapskite field is enclosed by the curves *ce*, *er*, *rp*, *pn*, and *en*. Here again the line joining the point representing the com-



position of pure darapskite to the origin passes through the Glauber's salt and glaserite fields and not through that of darapskite. Darapskite also is therefore decomposed by water.

FIG. 1.

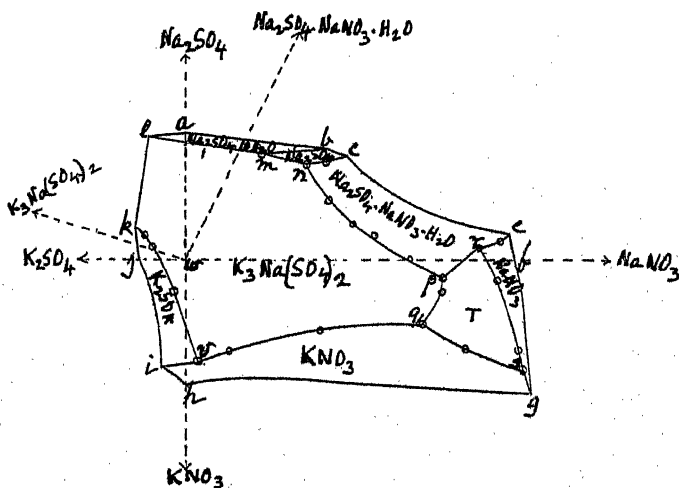
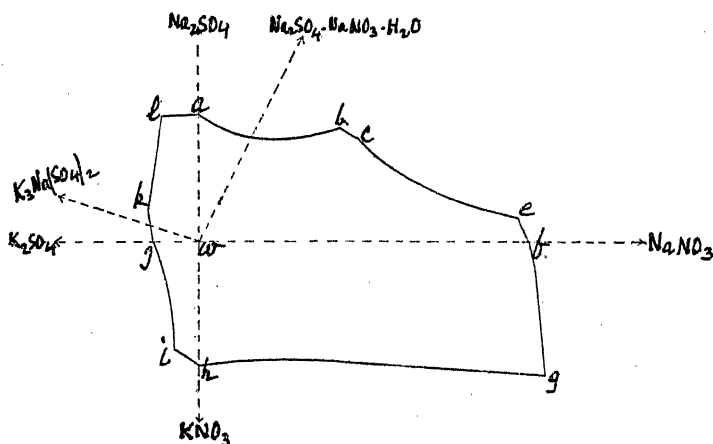


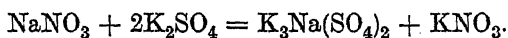
FIG. 2.

The quaternary saturation curves *er*, *rs*, and *sg* mark the inner boundary limit of the sodium nitrate field. The composition of the solution containing the maximum amount of potassium nitrate, which the ternary invariant solution *e* in contact with darapskite

and sodium nitrate can dissolve, is given by the point *s*. The same quaternary solution *s* is obtained when an excess of either sodium or potassium sulphate is added to the ternary invariant solution *g* in contact with excess of solid sodium and potassium nitrates.

The point *v* (Fig. 2) represents a quaternary invariant solution in equilibrium with three solid phases, potassium sulphate, glaserite and potassium nitrate. The composition of this solution, as will be seen from the position of the point *v* in Fig. 2, cannot be represented in terms of the solid phases with which it is in equilibrium. This solution is therefore incongruently saturated.

On the addition of sodium nitrate to the solution *v* in contact with glaserite, potassium sulphate and potassium nitrate, the following reaction occurs :



This reaction does not affect the composition of the quaternary invariant solution *v*, so long as there is any solid potassium sulphate present in contact with the solution. When so much of the sodium nitrate has been added that the whole of the solid potassium sulphate which was present in contact with the solution *v* is converted into glaserite and potassium nitrate, it disappears as a solid phase and the system acquires a degree of freedom. The point representing the compositions of the monovariant quaternary solutions then traverses the curve *vg* on the additions of increasing quantities of sodium nitrate to the solution *v*. The two solid phases in equilibrium with all quaternary solutions, the compositions of which are represented by points on the curve *vg* between the points *v* and *g*, are glaserite and potassium nitrate. When so much of the sodium nitrate has been added that the composition of the quaternary solution is represented by the point *g*, a distinct halt occurs in the movement of the point representing the compositions of the quaternary solutions, and further additions of sodium nitrate do not change the composition of the solution *g*, so long as there is sufficient glaserite present in contact with it. It is the persistence of the constant composition of the solution at *g* in contact with solid glaserite and potassium nitrate with increasingly small additions of sodium nitrate that leaves no doubt as to *g* being an invariant point.

The above facts combined with the positions of the curves *np* and *pq* all point to the existence of a new solid phase in the quaternary system. Before describing the various attempts that have been made to determine the nature of this new solid phase, we shall summarise the meanings of the various curves and surfaces in the

quaternary isotherm at 25°. The letter T stands for the new solid phase.

<i>almb</i>	is the saturation field of	Glauber's salt.
<i>bcnm</i>	" " "	sodium sulphate.
<i>cnpre</i>	" " "	darapskite.
<i>efgsr</i>	" " "	sodium nitrate.
<i>rpqs</i>	" " "	T
<i>gsqvih</i>	" " "	potassium nitrate.
<i>kgiv</i>	" " "	potassium sulphate.
<i>klmnpqv</i>	" " "	glaserite and solid solutions of glaserite and sodium sulphate.

#### Quaternary curves :

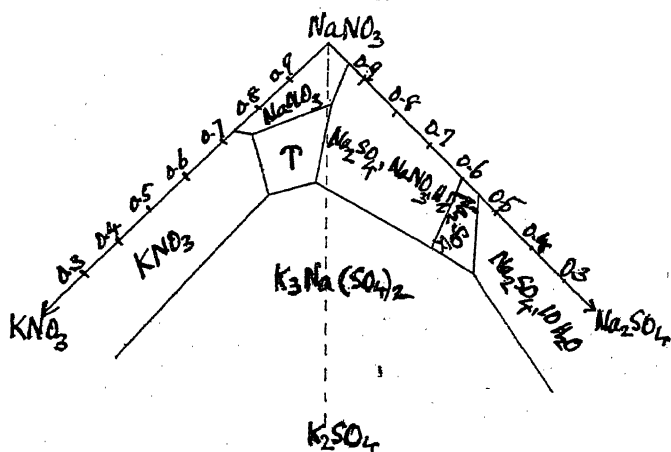
<i>bm</i>	is the saturation curve of	Glauber's salt and sodium sulphate.
<i>lm</i>	" " "	Glauber's salt and glaserite.
<i>mn</i>	" " "	sodium sulphate and glaserite.
<i>cn</i>	" " "	sodium sulphate and darapskite.
<i>np</i>	" " "	darapskite and glaserite.
<i>er</i>	" " "	darapskite and sodium nitrate.
<i>rp</i>	" " "	darapskite and the compound T.
<i>rs</i>	" " "	sodium nitrate and the compound T.
<i>gs</i>	" " "	sodium nitrate and potassium nitrate.
<i>sq</i>	" " "	potassium nitrate and the compound T.
<i>pq</i>	" " "	glaserite and the compound T.
<i>qv</i>	" " "	glaserite and potassium nitrate.
<i>iv</i>	" " "	potassium sulphate and potassium nitrate.
<i>kv</i>	" " "	potassium sulphate and glaserite.

The saturation curves and surfaces intersect in points representing solutions which are saturated with three solids. These quaternary invariant points are *m*, *n*, *p*, *q*, *r*, *s*, and *v*. The actual compositions of these solutions as well as the solids with which they are in equilibrium will be found in Table I.

*The Nature of the Phase T.*—The improbability of the existence of any compound other than darapskite of sodium sulphate and sodium nitrate has been pointed out in Part I. The positions of the various quaternary invariant points and those of the quaternary saturation curves and the existence of the enclosed area *rpqs* in Fig. 2 point clearly to the formation of a definite compound in the quaternary system. That this is essentially a quaternary compound, a triple or a tetragenic double salt, is indisputable. Attempts to isolate it by the evaporation of unsaturated solutions have proved fruitless. It will be seen by reference to Fig. 2 that points in the area *rpqs* represent solutions which are saturated with one solid only, viz., the compound T. The points representing the compositions of unsaturated solutions which will deposit this compound on isothermal evaporation as the first solid also project on to this area in the orthogonal projection. The compositions of all such unsaturated solutions which will deposit T as the first solid on evaporation cannot be read directly from this projection. Jänecke's method of representation ("Gessättigte Salzlösungen") is of inestimable value

for this purpose. A part of the Jänecke diagram is shown in Fig. 3. The proportions of dry salts contained by an unsaturated solution which will deposit T as the first solid on evaporation can be read from this figure at a glance. To hasten the process of evaporation, such mixtures of dry salts were dissolved in excess of water and the unsaturated solutions evaporated at higher temperatures to such an extent that when cooled to  $25^\circ$  they were expected to deposit T as the first solid. This method of procedure unfortunately suffers from the serious defect that the solubility of sodium sulphate in solutions of potassium and sodium nitrates decreases with rise of temperature and consequently sodium sulphate is deposited at

FIG. 3.

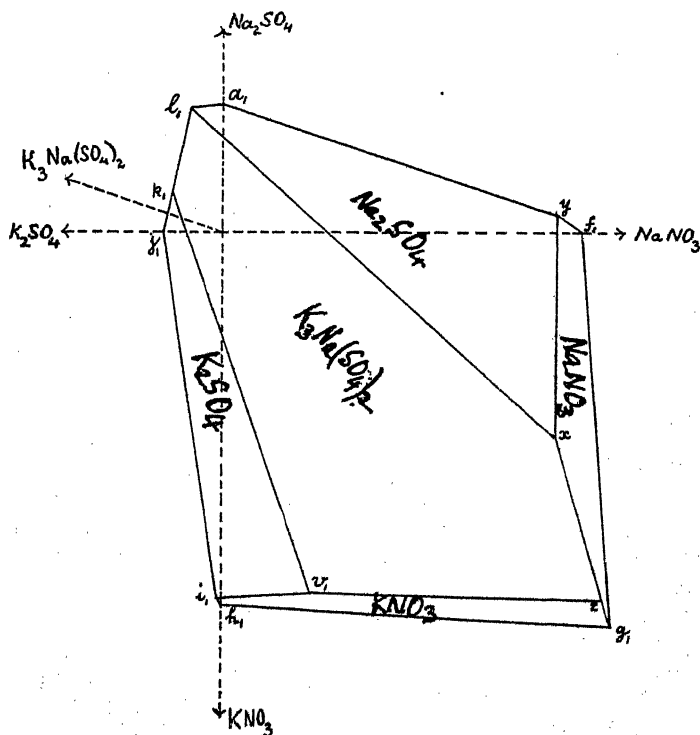


higher temperatures from solutions which are not saturated at  $25^\circ$  with respect to this salt. This fact makes it very difficult to adjust the whole course of evaporation in such a way that when the hot solution is cooled to  $25^\circ$  it should deposit T. Actually all such attempts have resulted in solutions, the compositions of which lie very near to the point *s* (Fig. 2), which is undoubtedly the crystallisation end-point of the system. In the isothermal evaporation at  $25^\circ$ , the solution remains supersaturated for a considerably long time. In all these cases of evaporation it has been found that crystallisation starts after the process of evaporation has been carried too far. This tendency to form supersaturated solutions has been noticed by van 't Hoff in many cases, particularly those of kieserite, leonite and kainite ( $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ ) ("Zur Bildung der organischen Salzablagerungen," 1905, 1, 28). The present case seems analogous to these and requires similar handling which

necessitates the measurements of the vapour pressure of the hydrated double salt, darapskite, as well as those of the saturated solutions at this temperature (*op. cit.*).

*The Isotherm at 90°.*—The isotherm at 90° is not so complicated as that at 25°. The only double salt that occurs in the system at this temperature is glaserite. All others seem to break down at temperatures below 90°. In the ternary systems, only the invariant points have been determined, and although the ternary curves have

FIG. 4.



not been followed completely, it is probable that in most cases they are not very different from straight lines. Furthermore, as the quaternary curve  $l_1x$  is practically a straight line, there is no doubt that the hydrated double salt, darapskite, in the ternary system  $H_2O-Na_2SO_4-NaNO_3$  and the compound T in the quaternary system split up into the simple salts at temperatures lower than 90°. The isotherm is shown in Fig. 4 as the orthogonal projection of the space model, and the data for the system at this temperature are in Table II in terms of molar percentages.

TABLE II.

*The System*  $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{NaNO}_3-\text{K}_2\text{SO}_4-\text{KNO}_3$  *at*  $90^\circ$ .

Composition in molar percentages.

Point.	$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2(\text{NO}_3)_2$ .	$\text{K}_2\text{SO}_4$ .	$\text{K}_2(\text{NO}_3)_2$ .	Solid phases.
$\alpha_1$	5.13	—	—	—	$\text{Na}_2\text{SO}_4$
$l_1$	4.98	—	1.25	—	$\text{Na}_2\text{SO}_4 + \text{D}_2$
	1.39	4.72	2.19	—	"
	—	6.65	2.04	0.41	"
$x$	—	14.29	0.64	8.34	$\text{Na}_2\text{SO}_4 + \text{D}_2 + \text{NaNO}_3$
$y$	0.71	13.72	—	—	$\text{Na}_2\text{SO}_4 + \text{NaNO}_3$
$f_1$	—	14.67	—	—	$\text{NaNO}_3$
$g_1$	—	15.81	—	16.02	$\text{NaNO}_3 + \text{KNO}_3$
$z$	—	16.20	0.70	14.96	$\text{NaNO}_3 + \text{KNO}_3 + \text{D}_2$
	—	12.17	0.67	14.78	$\text{KNO}_3 + \text{D}_2$
$h_1$	—	—	—	15.26	$\text{KNO}_3$
$i_1$	—	—	0.16	14.89	$\text{KNO}_3 + \text{K}_2\text{SO}_4$
$j_1$	—	—	2.37	—	$\text{K}_2\text{SO}_4$
$k_1$	1.49	—	1.97	—	$\text{K}_2\text{SO}_4 + \text{D}_2$
$v_1$	—	4.16	0.59	14.78	$\text{K}_2\text{SO}_4 + \text{D}_2 + \text{KNO}_3$



The author is indebted to Professor F. G. Donnan for his very kind help and interest during the progress of this work.

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### XXXII.—*Preparation, Hydrolysis and Reduction of the Fluoro-, Chloro-, and Bromo-benzyl Bromides.*

By JOHN BALDWIN SHOESMITH and ROBERT HENRY SLATER.

IN previous communications (J., 1922, 121, 1392; 1923, 123, 2828; 1924, 125, 1312, 2278) an account was given of the manner in which the reactivity of halogen atoms in various halogenated benzenoid derivatives is influenced by oxygen and by the hydrogen of a methyl group. The investigations have been continued with a view to discovering the effect of fluorine, chlorine, and bromine in such compounds. From the point of view of the principle of induced alternate polarities the halogens, except fluorine, appear to act as weakly negative "key-atoms" (as pointed out by Lapworth, *Mem. Manchester Phil. Soc.*, 1920, 64, No. 3). The present investigation has shown that (1) fluorine is capable of inducing differences of reactivity very similar to, but smaller than those met with in the cases of the methoxybenzyl bromides (J., 1922, 121, 1392) and the  $\alpha$ -bromoxylenes (J., 1924, 125, 2278) and (2) chlorine and bromine induce still smaller differences, and the chloro- and bromo-benzyl bromides provide the first examples encountered in this series, in

which a change of reagent does not cause a change in the order of reactivity.

The order of ease with which the bromides lose their bromine as bromidion in solution in aqueous alcohol is: (1) *p*-fluorobenzyl bromide > benzyl bromide > *o*-fluoro- > *m*-fluoro-; (2) benzyl bromide > *p*-chloro- > *o*-chloro- > *m*-chloro-; (3) benzyl bromide > *p*-bromo- > *o*-bromo- > *m*-bromo-. The order of ease of reduction by hydriodic acid is: (1) *o*-fluoro- > *m*-fluoro- > benzyl bromide > *p*-fluoro-; (2) *o*-chloro- > *p*-chloro- > *m*-chloro- > benzyl bromide; and (3) *o*-bromo- > *p*-bromo- > *m*-bromo- > benzyl bromide. The differences of ease of hydrolysis are quite marked. Those of ease of reduction are small, but several repetitions of the experiments led to the same order of reactivity and, as is seen from the above, the order of ease of reduction of the chloro- and bromo-compounds is not analogous to that discovered in the cases of the methoxybenzyl bromides, the *o*-bromoxylenes, and the fluorobenzyl bromides.

A series of experiments was undertaken to see if this non-reversal of the order of reactivity is due to any of the following causes: (a) removal of halogen from the nucleus, (b) liberation of iodine as follows: (1)  $\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{Br} + \text{HI} \rightarrow \text{R}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{I} + \text{HBr}$ . (2)  $2\text{R}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\text{I} \rightarrow \text{R}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{R}$  (compare Silberrad, J., 1924, 125, 2196), and (c) the more rapid formation of the iodide in the case of the para-isomerides and subsequent reduction of the iodides by hydriodic acid. The bromides were reduced for a long time, but the slight elimination of nuclear halogen then noted was not sufficient to reverse the discovered order of reactivity when correction was made for it. Reaction (2) is a photochemical one and does not take place in a dark thermostat such as was used in these experiments. In order to test (c), the bromobenzyl iodides were prepared; they were reduced by hydriodic acid at the same rate as the corresponding bromides. Thus it appears as if the conversion of the bromide into iodide is due to a mass-action effect and, owing to the concentration of hydriodic acid used, goes almost equally rapidly in all cases. Some of the iodides lose iodine more rapidly than their isomerides, and when a change in order of reactivity with change of reagent takes place alternating polar influences are very strong, *e.g.*, in the methoxybenzyl bromides.

An approximate estimate of the magnitude of the three influences which affect the reactivity of the bromine atom in the bromides, namely, the general (represented by *g*), the alternating (represented by *a*), and the so-called steric influence (represented by *s*), may be arrived at from considerations similar to those put forward by Flürscheim (J., 1909, 95, 726). A comparison by means of reaction velocities, which is the most satisfactory method, is impossible,

because only during the hydrolysis of *o*- and *m*-fluorobenzyl bromides and also of the isomeric nitrobenzyl bromides (Shoesmith and Hetherington, J., 1924, 125, 1316) were the reactions slow enough to give monomolecular velocity coefficients. The reduction of the bromides, moreover, is not the simple bimolecular reaction investigated by West in the case of bromomalonyl compounds (J., 1924, 125, 710). The reciprocals of the times taken for half-completion of the reaction in the various cases may be used to obtain the necessary comparison.

If  $K_o$ ,  $K_m$ ,  $K_p$  and  $K_u$  represent the reciprocals of the times taken for half-completion of the reactions for the ortho-, meta-, para- and unsubstituted compounds, respectively, the manner in which the velocities of the reactions are affected by the three influences mentioned above may be expressed by the following equations: \*

$$\log_{10} K_o = \log_{10} K_u + g + a + s.$$

$$\log_{10} K_m = \log_{10} K_u + g - a.$$

$$\log_{10} K_p = \log_{10} K_u + g + a,$$

and hence

$$g = \frac{1}{2}(\log_{10} K_m + \log_{10} K_p - 2 \log_{10} K_u),$$

$$a = \frac{1}{2}(\log_{10} K_p - \log_{10} K_m),$$

and  $s = \log_{10} K_o - \log_{10} K_p.$

Obtained from graphs plotted from observations recorded in this and previous communications, the reciprocals of the various times taken for half-hydrolysis (*x*) and half-reduction (*y*) at the temperatures stated are summarised in Table I, on which the following remarks are based:

*The general effect.* The order in which the atoms or groups affect the reactivity of the bromine (*a*) towards hydrolysing agents in a general way is OMe, Me, F, Cl, Br, CO<sub>2</sub>H, NO<sub>2</sub>, ranging from the strongly enhancing methoxy-group to the strongly retarding nitro-group, and (*b*) towards hydrogen iodide is OMe and Me, Cl, Br, CO<sub>2</sub>H, and F. In the latter case, only the methoxy- and the methyl-group have an appreciable general influence on the reduction velocity. The strong general influence of the methoxy-group is noteworthy.

*The alternating effect.* The order in which alternation towards hydrolysing agents is produced is similar to that given above (*a*); in this case, however, the magnitudes of the effect may be compared. The order is OMe > F > Me > Cl > Br > CO<sub>2</sub>H > NO<sub>2</sub>. The differences observed in the first five cases, *i.e.*, negative groups, have positive values, whilst in the last two, *i.e.*, positive groups, they have negative values. For reduction, the order is OMe and Me > CO<sub>2</sub>H > F, Cl,

\* Logarithms are used in order that the expressions shall finally involve a product or a quotient as the case may be.



TABLE I.

Compounds.	$K_o$		$K_m$		$K_p$		$g$		$a$		$s$	
	$x$ .	$y$ .	$x$ .	$y$ .	$x$ .	$y$ .	Hyd.	Red.	Hyd.	Red.	Hyd.	Red.
Methoxybenzyl bromides.	<33.3 (60°)	0.107 (25°)	0.47	12.5	>33.3*	0.00	>1.54	+∞	0.92	-∞	nil	∞
$\omega$ -Bromoxylenes.	2.17 (60°)	>0.00 (25°)†	0.77	0.15	2.78	0.00	0.68	+∞	0.28	-∞	-0.11	∞
Fluorobenzyl bromides.	0.28 (60°)	0.00 (25°)	0.20	0.00	0.91	0.00	-0.39	-	0.33	-	-0.51	-
Fluorobenzyl bromides.	1.0 (76°)	0.27 (101°)	0.71	0.22	4.0	0.18	-0.22	0.00	0.37	-0.05	-0.6	0.18
Chlorobenzyl bromides.	0.85 (76°)	0.36 (101°)	0.65	0.24	1.8	0.31	-0.60	0.27	0.22	+0.05	-0.32	0.07
Bromobenzyl bromides.	0.84 (76°)	0.36 (101°)	0.71	0.23	1.43	0.29	-0.67	0.22	0.15	+0.05	-0.23	0.09
Nitrobenzyl bromides.	0.29 (76°)	-	0.33	-	0.29	-	-1.69	-	0.028	-	nil	-
$\omega$ -Bromotoluic acids.	-	-	0.72 (76°)	0.27 (110°)	0.56	0.65	-1.07	+0.06	0.055	+0.19	-	-
	Benzyl bromide $x = 0.67$ (60°), 2.17 (76°). $y = 0$ (25°), 0.20 (101°), 0.39 (110°).											

\* The extraordinary rapidity with which *p*-methoxybenzyl bromide is hydrolysed in aqueous alcoholic solution suggests that this figure should be much greater and hence *g* and *a* for hydrolysis approach those for reduction, *i.e.*, ∞

†  $\omega$ -Bromo-*o*-xylene is definitely but very slowly reduced at 25°. A definite value for  $K_o(g)$  cannot be given, but *s* (red.) must be large on account of the stability of  $\alpha$ -iodo-*p*-xylene at 25° in presence of hydrogen iodide.

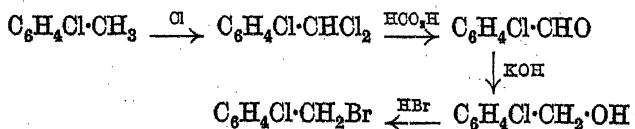
and Br. Here the differences in the cases of the OMe, Me and F compounds have positive values and in the other cases negative values. According to the principle of induced alternate polarities the sign of the difference is determined by the positive or negative character of the substituents, and the reduction of the chloro- and bromo-benzyl bromides is the only case so far met with in this series in which the sign of the difference is other than was expected.

*The steric effect.* The values obtained for  $s$  show that this effect in some cases diminishes and in other cases increases the reactivity, the former being observed in the hydrolyses, the latter in the reductions. Therefore the retarding of the reactions cannot be due to steric hindrance as normally conceived, and the results justify the conclusion that there is a disturbing factor governing the reactivity of ortho-compounds (see Lapworth and Shoesmith, J., 1922, 121, 1394).

The influence of atoms or groups of atoms having the same electronic shell may be compared also, since the manner in which the methyl and the methoxy-group and the fluorine atom each affect the reactivity of the bromine atom of the  $-C_6H_4 \cdot CH_2Br$  group has been investigated. The order of potency is  $OMe > Me > F$ , except in the case of alternation of hydrolysis, for which the order is  $OMe > F > Me$ .

#### EXPERIMENTAL.

*Preparation of the Isomeric Chlorobenzyl Bromides.*—The most reliable method of preparing the ortho- and para-isomerides is indicated by the scheme :



The appropriate chlorotoluene, mixed with 5% of its weight of phosphorus pentachloride, was chlorinated at 160° until the required increase in weight had taken place. The oil thus obtained was boiled with twice its bulk of 98% formic acid ( $d$  1.20) for  $\frac{1}{2}$  hour, the mixture poured into an excess of cold water, and the oil separated, dissolved in ether, washed twice with water, and once with aqueous sodium hydroxide. The aldehyde was precipitated as the bisulphite compound, which was carefully washed with ether, dissolved in water, and the pure aldehyde liberated by the addition of excess of sodium carbonate. It was converted into the alcohol (*o*., m. p. 70°; *p*., m. p. 72°) by treatment with 25% alcoholic potassium hydroxide, and this into the bromide by means of hydrogen bromide in benzene solution.

*o*-Chlorobenzyl Bromide is an oil, b. p.  $102^{\circ}/9$  mm. (Found: Br, 39.05.  $C_7H_5ClBr$  requires Br, 38.9%). *p*-Chlorobenzyl bromide has m. p.  $51^{\circ}$  (compare Jackson and Field, *Ber.*, 1878, 11, 905) (Found: Br, 38.7%).

*m*-Chlorobenzyl Bromide.—*m*-Nitrobenzaldehyde was converted into *m*-chlorobenzaldehyde (Erdmann and Schwechten, *Annalen*, 1890, 260, 59), b. p.  $213$ — $214^{\circ}$ , and this was reduced to the alcohol in alcoholic potassium hydroxide. The alcohol had b. p.  $242^{\circ}$ , not  $234^{\circ}$  as stated by Mettler (*Ber.*, 1905, 38, 1749), and from it *m*-chlorobenzyl bromide, an oil of b. p.  $109^{\circ}/10$  mm. (Found: Br, 38.8%), was obtained as before.

*The Isomeric Bromobenzyl Bromides.*—Each of these compounds was prepared by passing a stream of air through a weighed quantity of bromine into the appropriate, boiling bromotoluene. The product was distilled under diminished pressure, the portion passing over between  $120^{\circ}$  and  $140^{\circ}/12$ — $16$  mm. being collected, cooled, and when solid recrystallised from alcohol. The bromides thus obtained had m. p.'s: *o*-,  $31^{\circ}$ ; *m*-,  $40^{\circ}$ ; and *p*-,  $63^{\circ}$  [Found: hydrolysable Br, (*o*-) 32.1, (*m*-) 31.8, (*p*-) 31.8. Calc. for  $C_7H_7Br_2$ , hydrolysable Br, 32.0%] (compare Jackson, *Ber.*, 1876, 9, 932).

The *isomeric bromobenzyl iodides* were prepared by boiling aqueous acetone solutions of the corresponding bromides with rather more than the calculated quantity of potassium iodide for  $\frac{1}{2}$  hour. The mixture was then poured into water, and the iodide recrystallised from light petroleum. *o*-Bromobenzyl iodide crystallises in shining, white needles, m. p.  $47^{\circ}$  (Found: I, 42.75.  $C_7H_5BrI$  requires I, 42.7%). *m*-Bromobenzyl iodide crystallises in white, six-sided prisms, m. p.  $42^{\circ}$  (Found: I, 42.8%). *p*-Bromobenzyl iodide crystallises in white needles, m. p.  $73^{\circ}$  (Hantzsch and Schultze, *Ber.*, 1896, 29, 2253, give  $80$ — $81^{\circ}$ ) (Found: I, 42.9%).

[With R. H. SLATER.]

*Preparation of the Isomeric Fluorotoluenes.*—A solution of the requisite toluidine (25 g.) in a mixture of 30 c.c. of concentrated sulphuric acid and 80 c.c. of water was cooled to  $-5^{\circ}$  and diazotised with 20 g. of sodium nitrite dissolved in 50 c.c. of water, the temperature being kept below  $5^{\circ}$ . The solution of the diazotised base was added to about 400 c.c. of commercial hydrofluoric acid (50—60%) in a 1,500 c.c. brazed spun-copper flask surrounded by ice, after which the flask was fitted, by means of a cork, with a copper reflux condenser and very carefully warmed on a water-bath for about an hour (alternatively, the mixture may be left at room temperature for about 16 hours). The condenser was then reversed and the flask heated directly. The mixture of fluorotoluene, hydrofluoric acid,

and cresol that distilled was collected in a copper beaker containing 300 c.c. of 30% aqueous sodium hydroxide solution surrounded by a good freezing mixture. When all the fluorotoluene had distilled, the alkaline mixture in the beaker was extracted thrice with ether, the combined extracts were de-emulsified by saturated ammonium sulphate solution and dried over anhydrous sodium sulphate, and the ether was evaporated. In each case the fluorotoluene distilled at 113–118° and the yield was 15–16 g. (65%) (compare Holleman and Beekman, *Rec. trav. chim.*, 1904, 23, 238).

*Preparation of the Isomeric Fluorobenzyl Bromides.*—Each fluorotoluene (80 g. in four lots) was brominated by volatilising bromine (30 g.) in a slow stream of dry air and passing the vapour into the boiling fluorotoluene (20 g.); by using small quantities nuclear substitution was avoided. The brominated oil was boiled with formic acid (*d* 1.20; *ca.* 2 vols.) for 6 hours, fluorobenzotribromide and fluorobenzylidene bromide being thus converted into fluorobenzoic acid and fluorobenzaldehyde, respectively, and some of the fluorobenzyl bromide into fluorobenzyl alcohol. The mixture was poured into a large excess of water, and the oil was separated, and washed in ethereal solution with 10% aqueous sodium hydroxide until free from fluorobenzoic and formic acids. After complete removal of the fluorobenzaldehyde with freshly prepared sodium bisulphite solution—the aldehydes and the benzyl bromides form constant-boiling mixtures—the ethereal solution was dried over anhydrous sodium sulphate, and the ether distilled. The residual oil was saturated in benzene solution with dry hydrogen bromide to convert any fluorobenzyl alcohol into the bromide, and after the removal of the benzene the fluorobenzyl bromide was fractionally distilled in a vacuum in the apparatus described by Widmer (*Helv. Chim. Acta*, 1924, 7, 52). *o*-Fluorobenzyl bromide had b. p. 84–85°/15 mm.; *m*-fluorobenzyl bromide, 77°/12 mm.; and *p*-fluorobenzyl bromide, 85°/15 mm. [Found: Br, 42.4 (*o*-); 42.0 (*m*-); 42.1 (*p*-).  $C_7H_5FBr$  requires Br, 42.3%].

*Hydrolysis of the Bromides.*—Twenty c.c. of a standard solution (105 c.c.) of the bromide in absolute alcohol were placed in a standard 25 c.c. flask, 5 c.c. of water added, and the volume was made exactly 25 c.c. by adding absolute alcohol. The whole was thoroughly mixed, immersed in the vapour of boiling carbon tetrachloride for a definite time, and then poured into a large volume of water. The liberated hydrobromic acid was titrated directly with standard aqueous sodium hydroxide and methyl-red. The results are in Table II, where *w* represents the total weight of benzyl bromide used, *x* the percentage changed, and *t* the time of hydrolysis in hours.

TABLE II.

	Ortho-compounds.			Meta-compounds.			Para-compounds.		
F :	$w = 0.5218$ g.			0.5456 g.			0.5102 g.		
Cl :	0.5600 „			0.5441 „			0.5418 „		
Br :	0.6702 „			0.6600 „			0.6693 „		
	$\alpha$ .			$\alpha$ .			$\alpha$ .		
$t$ .	F.	Cl.	Br.	F.	Cl.	Br.	F.	Cl.	Br.
$\frac{1}{2}$	25	25	24	24	21	21	68	45	40
1	51	46	44	41	38	39	88	69	62
2	76	68	66	63	58	60	96	88	85
4	94	88	87	86	80	82	98	96	95
8	95	96	96	94	92	95	99	98	98

In Table III are results obtained in a similar manner in order to compare the hydrolysis of benzyl bromide, *m*-methoxybenzyl bromide,\* the fluorobenzyl bromides, and the  $\omega$ -bromoxylenes at 60.5° (b. p. of chloroform).

TABLE III.

	Fluorobenzyl bromides.			<i>m</i> -Methoxybenzyl bromide.	Benzyl bromide.
$w$ .	$o$ . 0.5240	$m$ . 0.5252	$p$ . 0.5102	0.543	0.4610
$t$ .	$\alpha$ .	$\alpha$ .	$\alpha$ .	$\alpha$ .	$\alpha$ .
$\frac{1}{2}$	9	7	26.5	14	22
1	20	11	48	29	39
2	33	23	69	49	59
4	56	41	90	72	80
8	76	63	95	88	88
16	91	81	96	—	—

*Reduction of the Bromides.*—Reduction at 25° under the conditions described by Lapworth and Shoesmith and by Shoesmith and Slater (*loc. cit.*) being so slow that satisfactory results could not be obtained, the bromides were reduced in a thermostat at 101°. Ten c.c. of a standard solution of the bromide in 50 c.c. of glacial acetic acid were placed in the 25 c.c. standard flask, 10 c.c. of freshly distilled hydriodic acid ( $d$  1.680) added, the volume was made up to 25 c.c. with glacial acetic acid, and the whole thoroughly mixed, and kept in the thermostat for a definite time. The percentage reduction was then estimated as in previous cases.

The concentration of the hydriodic acid and the amount of iodine in it both influence the rate of reduction, and therefore a series of reductions was carried out on the same day with the same hydriodic acid. The results are in Table IV,  $t$  and  $\alpha$  having the same significance as before.

\* At all temperatures, in aqueous alcoholic solution, *p*-methoxybenzyl bromide is completely, and the *o*-compound almost completely, hydrolysed in 2½ minutes.

TABLE IV.

t.	Ortho-compounds.			Meta-compounds.			Para-compounds.		
	x.			x.			x.		
	F.	Cl.	Br.	F.	Cl.	Br.	F.	Cl.	Br.
1½	29.5	32	30 (31)	23	23	23 (21)	22.5	28	26 (27)
3	45	53	53 (54)	37	43	43 (41)	34	49	47 (47)
6	65	76	74 (76)	63	64	61 (60)	57	68	64 (65)

Benzyl bromide :  $x = 25, 38,$  and  $61$  for  $t = 1\frac{1}{2}, 3,$  and  $6$ , respectively.

The figures in brackets represent the reduction of the bromobenzyl iodides. In Table V are the results of reductions of the bromides made at a higher temperature ( $110^\circ$ ) in order to determine the amount of nuclear halogen eliminated.

TABLE V.

t.	Ortho-compounds.		Meta-compounds.		Para-compounds.	
	x.		x.		x.	
	Cl.	Br.	Cl.	Br.	Cl.	Br.
2	76	77	57	57	70	72
4	91	91	81	79	88	88
8	102	100	97	97	98	97
18	104	103	100	100	101	101

*p*-Chlorobenzyl iodide (m. p.  $65^\circ$ ) was isolated from the reaction of *p*-chlorobenzyl bromide and hydrogen iodide in glacial acetic acid at  $25^\circ$  (compare Shoesmith and Slater, *loc. cit.*), but, owing to the dilution at which the reductions had to be carried out, end-products in the other cases could not be separated. The figures obtained, however, show that the reaction in the cases of the meta- and para-isomerides was quite normal in that it first involved conversion of the bromide into iodide and subsequent reduction of this to the halogenated toluene.

The iodobenzyl bromides have not been examined, since in a former communication we showed that hydrogen iodide reduces iodo-toluene to toluene.

The authors gratefully acknowledge the many valuable suggestions made by Dr. W. O. Kermack, especially with regard to the formulæ on pp. 216, and the receipt of a grant from the Earl of Moray Research Fund. They also thank the Trustees of the Carnegie Trust for the Universities of Scotland for a scholarship which enabled one of them (R. H. S.) to take part in this research.

### XXXIII.—*Cyclic Organo-metallic Compounds. Part I.* *Compounds of Tellurium.*

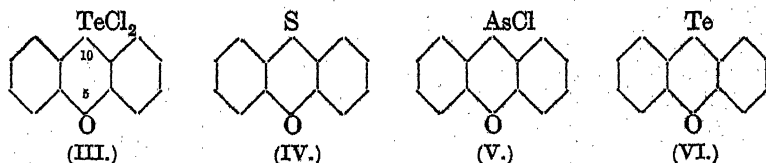
By HARRY DUGALD KEITH DREW.

THE present work has for its object the investigation of cyclic organo-metallic compounds (*i.e.*, compounds in which a metallic atom is united directly to carbon atoms, taking part therewith in ring formation), few of which have hitherto been synthesised.

Tellurium tetrachloride and diphenyl ether slowly but almost completely condense when heated together in chloroform solution. Hydrogen chloride is evolved and a yellow telluritrichloride is formed in which the group  $-\text{TeCl}_3$  has replaced a hydrogen atom of one of the aromatic nuclei. This substance is *p*-phenoxyphenyl-telluritrichloride (I),  $\text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{TeCl}_3$ , since on reduction with aqueous potassium metabisulphite it becomes transformed to a purplish-red, crystalline substance, *pp'*-diphenoxydiphenyl ditelluride (II),  $\text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{Te}:\text{Te}\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ , which shows a normal molecular weight in freezing benzene.

The formation of these substances demonstrates that the tellurium atom can be caused to enter an aromatic nucleus without the aid of Grignard reagents (compare Morgan and Drew, J., 1925, 127, 2307). That the group  $-\text{TeCl}_3$  enters the aromatic nucleus almost exclusively in one position was shown by the absence of an isomeric telluritrichloride from the by-products of this condensation and by the homogeneity of the ditelluride resulting upon reduction.

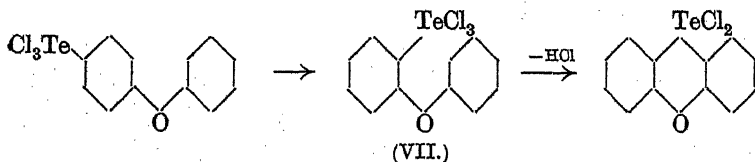
The telluritrichloride (I) melts at  $156^\circ$ , but if it is heated to about  $200^\circ$  a further (intramolecular) condensation occurs; a molecule of hydrogen chloride is evolved, and a colourless, crystalline, cyclic compound, 10:10-dichlorophenoxytellurine (III), is produced. That this substance contains the tellurium atom in a di-ortho-position relatively to the oxygen atom is indicated both from stereochemical considerations and by the existence of structurally analogous compounds of sulphur (IV) and of arsenic (V), of which the constitutions must be regarded as established (compare, for



example, Turner and Sheppard, J., 1925, 127, 544). Additional evidence upon this point is afforded by the ready reduction of the telluridichloride (III) to a yellow, crystalline, cyclic substance, phenoxytellurine (VI), of such marked chemical and physical stability

that there seems no doubt as to the nature of its tricyclic structure. This substance, which shows a normal molecular weight in freezing benzene, resembles somewhat closely the colourless sulphur analogue, phenoxthin or phenothioxin (IV; Mauthner, *Ber.*, 1906, 39, 1344), in both physical and chemical properties. It has, for example, a delicate floral odour suggesting rose-water, whereas phenoxthin is described as having a geraniol smell; and both substances develop intense colorations with concentrated sulphuric acid. Phenoxtellurine readily adds on bromine or iodine in chloroform solution, yielding primrose-yellow 10 : 10-dibromophenoxtellurine and red 10 : 10-di-iodophenoxtellurine, respectively; while the action of warm nitric acid converts it into colourless phenoxtellurine 10 : 10-dinitrate.

The formation of a cyclic tellurium compound from the telluritrichloride (I) suggests that the latter must in reality be the *o*-compound (VII). Since, however, it has been shown (Morgan and Drew, *loc. cit.*) that in the analogous condensation with phenetole the group  $-\text{TeCl}_3$  takes up exclusively a para-position with respect to ethoxyl, a para-orientation with respect to the phenoxy-group in the present case also would be anticipated. There remains thus the probability that the telluritrichloride is actually the *p*-compound (I), and that, on being heated above its melting point, it suffers a preliminary isomeric change into the *o*-compound (VII), which can then undergo the inner condensation :—



In an endeavour to test this possibility, the action of concentrated nitric acid upon the ditelluride (II) was tried. The telluritritrate,  $\text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{Te}(\text{NO}_3)_3$ , was first produced and then the tellurium atom displaced, *pp'*-dinitrodiphenyl ether (m. p.  $143^\circ$ ) being formed; no *o*-nitro-compound was isolated. Of the two obvious mechanisms of displacement of the tellurium atom, *viz.*,

(1)  $\text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{Te}(\text{NO}_3)_3 + \text{HO}\cdot\text{NO}_2 = \text{Te}(\text{NO}_3)_3\cdot\text{OH} + \text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ,  
and (2)  $\text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{Te}(\text{NO}_3)_3 + \text{H}\cdot\text{NO}_3 = \text{Te}(\text{NO}_3)_4 + \text{PhO}\cdot\text{C}_6\text{H}_5$ ,  
the more probable would appear to be (1); and, if this is the case, the production of a *p*-nitro-compound of diphenyl ether proves the structure of the telluritrichloride and of the ditelluride derived from it. The possibility of mechanism (2), in which diphenyl ether is first liberated and then nitrated, cannot, however, be ignored with safety.



On the whole, the weight of evidence seems to be in favour of the para-structure; and accordingly it is considered best to adopt, for the present, the formulæ I and II for the telluritrichloride and ditelluride respectively, and to assume the transformation of the *p*-telluritrichloride into its *o*-isomeride as an intermediate step in the synthesis of the cyclic dichloride (III).

The best method of preparing 10:10-dichlorophenoxtellurine, giving a yield of 50%, is to heat at about 200° a mixture of tellurium tetrachloride and diphenyl ether in molecular proportions. The reaction proceeds in two stages, marked evolution of hydrogen chloride occurring first near 120° and then again near 200°. These stages apparently represent respectively the formation of the telluritrichloride and its transformation to the cyclic telluridichloride. The hypothetical preliminary isomeric change of the *p*- to the *o*-telluritrichloride must then occur between the temperature of the melting point of the telluritrichloride and the higher temperature, *i.e.*, between about 160° and 200°, a separate experiment having shown that the presence of chloroform in the preliminary stages of the above reaction had no effect upon the nature of the ultimate product.

Accordingly, an attempt was made to isolate the *o*-telluritrichloride by heating the supposed *p*-telluritrichloride to about 160° in an atmosphere of nitrogen. From the glassy product, which was a complex mixture containing a proportion of regenerated tellurium tetrachloride, a substance was obtained which had the properties of a telluritrichloride and yet was not identical with the initial material. This compound, which crystallised from benzene in almost colourless, pearly flakes decomposing at 125°, was possibly the *o*-telluritrichloride (VII), since it was easily reduced to a red substance possessing the characteristics of a ditelluride. Neither of these compounds was obtained in a pure condition, however, and their identity with the above structures has not been definitely established.

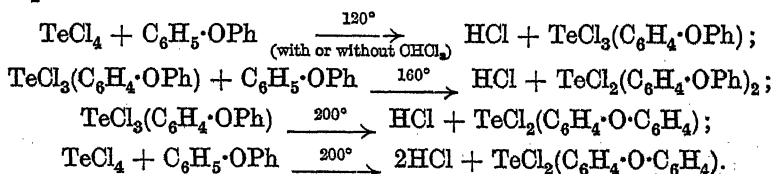
A colourless non-cyclic telluridichloride occurs as a by-product in the condensation of tellurium tetrachloride and diphenyl ether in chloroform solution; and this substance results also when the telluritrichloride (I) is heated with an excess of diphenyl ether at about 160°, hydrogen chloride being set free. This telluridichloride must therefore be *pp*-diphenoxydiphenyltelluridichloride (VIII),  $\text{PhO}\cdot\text{C}_6\text{H}_4\cdot\text{TeCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ .

Here again the di-para-orientation is considered the more probable, since the substance is formed in small amount even at the low temperature of a condensation in chloroform. Owing, however, to the uncertainty attaching to the conditions under which the hypothetical

change of the tellurium atom from the *p*- to the *o*-position occurs, a di-ortho-, or even a para-ortho-structure is not definitely excluded.

The non-cyclic telluridichloride (VIII) was unchanged by the action of heat at 210°, and its formation was therefore unconnected with the production of the cyclic telluridichloride (III). It was of interest, therefore, to find that the latter was the main product of the action of heat at 200° upon a mixture of tellurium tetrachloride and a large excess (3½ mols.) of diphenyl ether, for this result seems to supply further evidence in favour of the hypothetical isomeric change of the *p*- to the *o*-telluritrichloride; since, in the absence of this transformation, it would be expected that the whole of the telluritrichloride would be changed at 200° into the non-cyclic telluridichloride (VIII), a reaction which is fairly rapid even at 160°. The production of the *o*-telluritrichloride must therefore accelerate rapidly at temperatures approaching 200°.

Leaving aside the question of orientation, we have thus the following series of changes which have been realised experimentally, with the temperatures at which the reactions are appreciably rapid :—



It is probable that *pp'*-diphenoxydiphenyltelluridichloride (VIII) is always formed, at least in minor quantities, when tellurium tetrachloride and diphenyl ether are heated together; but this telluridichloride is not readily separated from the resinous or colloidal by-products associated with it in the reaction-mixture.

Attempts are being made to clear up the uncertainty which exists regarding the orientations of the foregoing substances; and, in addition, the author is investigating the analogues and derivatives of phenoxytellurine and similar compounds containing other metals and metalloids.

#### EXPERIMENTAL.

*Condensation of Tellurium Tetrachloride with Diphenyl Ether in presence of Chloroform.*—Four experiments were carried out, with proportions of diphenyl ether ranging from 1 to 1½ mols. per mol. of tellurium tetrachloride and with amounts of chloroform varying between 0.6 and 2 c.c. per g. of the tetrachloride; the times of heating were between 8 and 26 hours. The optimum experiment only will be described in detail: 23.8 g. of tellurium tetrachloride, 18.7 g.

( $1\frac{1}{2}$  mols.) of diphenyl ether, and 15 c.c. of dry chloroform were heated under reflux during 26 hours, moist air being excluded. Hydrogen chloride was evolved and all the tellurium tetrachloride dissolved in about  $1\frac{1}{2}$  hours. The yellow trichloride that was gradually deposited from the intensely orange-brown solution was recrystallised from boiling dried chloroform; the mother-liquor on concentration to a syrup gave further crops of trichloride, which were recrystallised as before (total yield, 31.5 g. or 90%). The final syrup, on long standing in a desiccator, gave the dichloride (0.5 g.) in large, colourless prisms, which were recrystallised from ethyl alcohol or acetone. In this and in other experiments the separating trichloride was practically pure. Portions of it were subjected to careful fractionation from boiling dry chloroform, in an attempt to detect the presence of a possible isomeric trichloride. The melting points and mixed melting points of the recrystallised first and final fractions were always practically identical. Slight differences sometimes observed were traced to the presence of small amounts of the dichloride.

*p*-Phenoxyphenyltelluritrichloride (I) separates from its yellow solution in chloroform or carbon tetrachloride in opaque, nodular rosettes of very small, pale yellow needles. The rosettes crumble, on drying, to a creamy yellow, crystalline powder. The substance melts at  $156$ — $157^{\circ}$  to a transparent, yellow liquid, but never quite sharply, usually softening from about  $154^{\circ}$ , behaviour which suggests a partial change near the melting point. The compound is almost insoluble in light petroleum, sparingly soluble in hot carbon tetrachloride, but more soluble in hot chloroform or benzene. It is readily hydroxylated by water or hydroxylic organic solvents (Found: C, 35.6; H, 2.3; Cl, 26.6.  $C_{12}H_9OCl_3Te$  requires C, 35.75; H, 2.25; Cl, 26.4%).

pp'-Diphenoxydiphenyltelluridichloride (VIII), a by-product in the foregoing condensation, was best prepared by heating 3.9 g. (1 mol.) of the above trichloride and 1.7 g. (1 mol.) of diphenyl ether together at  $140$ — $165^{\circ}$  during 6 hours, moist air being excluded and a slow current of nitrogen maintained in the apparatus. Hydrogen chloride was evolved even at  $145^{\circ}$ . The hard, semi-crystalline mass was extracted with ether, the ether removed, and the resulting semi-solid triturated successively with light petroleum and ethyl alcohol, and filtered. There remained 2.8 g. of crude dichloride containing an amorphous impurity, readily soluble in chloroform, benzene or acetone, from which it was found difficult to free the dichloride. Purification was finally effected by fractional solution in cold benzene, followed by crystallisation of the least soluble fraction from benzene-light petroleum (b. p.  $40$ — $60^{\circ}$ ).

When two molecular proportions of diphenyl ether were employed and the heating was conducted during 10 hours at 115–150°, a similar product (1.1 g. from 1.5 g. of trichloride) was obtained, which yielded the dichloride on purification by means of carbon tetrachloride and ether. When quite pure, the dichloride separated from boiling methyl or ethyl alcohol in transparent, colourless, prismatic needles, which became slightly pink on keeping. The solutions in hot alcohol of impure specimens always became cloudy, on cooling, before crystallisation set in. The dichloride melted without decomposition at 157–158°, and depressed the almost identical melting point of the trichloride to about 120°. It was much more easily soluble than the trichloride in organic solvents, being readily soluble in cold benzene, chloroform or ether; but it was insoluble in light petroleum, and only moderately easily soluble in hot ethyl alcohol. The halogen atoms were firmly bound in this substance, which remained unaffected by cold aqueous potash, although it was decomposed by the boiling reagent with liberation of diphenyl ether (Found: Cl, 13.15.  $C_{24}H_{18}O_2Cl_2Te$  requires Cl, 13.2%).

When this dichloride was heated at 210° during an hour, it remained unchanged, no trace of diphenyl ether or of cyclic telluridichloride being produced.

*pp'-Diphenoxydiphenyl Ditelluride (II).*—The trichloride (7 g.) was reduced with 50 c.c. of ice-cold water and 11.6 g. (3 mols.) of powdered potassium metabisulphite, which was slowly added during  $\frac{3}{4}$  hour, the mixture being stirred mechanically. Sulphur dioxide was evolved, and a soft red mass produced. The reduction was completed by grinding the whole in a glass mortar during a further  $\frac{1}{2}$  hour. The deep purple, crystalline product was filtered off, washed with water, and dried in a vacuum; the yield of crude product (5.3 g.) was quantitative. The substance was then rapidly crystallised from hot light petroleum (b. p. 40–60°) saturated with sulphur dioxide, two crystallisations producing the analytically pure ditelluride. Careful examination of the mother-liquors failed to reveal the presence of an isomeride.

*pp'-Diphenoxydiphenyl ditelluride* separates from petroleum or alcohol in clusters of minute, bronzed, brownish-violet or purplish-red needles, which dissolve in organic solvents to dark red solutions. It commences to soften at 85° and melts to a deep red liquid at 87–88°. It is easily soluble in benzene, chloroform, carbon tetrachloride, ether, or acetone, only moderately easily soluble in light petroleum or alcohol, and insoluble in water [Found: C, 48.55; H, 3.05; Te, 43.1; *M*, cryoscopic in benzene, 579 ( $c = 1.39$ ), 595 ( $c = 2.04$ ).  $C_{24}H_{18}O_2Te_2$  requires C, 48.55; H, 3.05; Te, 43.0%; *M*, 593].

Great difficulty was at first experienced in purifying this substance sufficiently for analysis. Although it crystallised well from ethyl or methyl alcohol and from acetone or ether, the crystals were persistently low in carbon content (Found: C, 47·6, 47·6, 47·5, 48·05; H, 3·1, 3·2, 3·1, 3·15%). Finally the impurity was isolated: it consisted of a white, amorphous oxide, which was slowly reduced by aqueous potassium metabisulphite or aqueous sulphur dioxide to the ditelluride. In solution the ditelluride slowly precipitates this oxide when exposed to the air. With bromine in cold chloroform solution the ditelluride reacts to form a yellow *bromide* melting near 180° and readily soluble in hot chloroform. This substance is probably the analogue of the trichloride, since it is again reduced to the ditelluride by aqueous alkali bisulphites. With warm concentrated nitric acid the ditelluride yields ultimately *pp'*-dinitrodiphenyl ether (needles from alcohol; m. p. 142—143°).

*Preparation of 10 : 10-Dichlorophenoxytellurine.*—(1) *Action of heat on p-phenoxyphenyltelluritrichloride.* The trichloride (1·4 g.) was heated gradually during 4½ hours, from 150° to 210°; hydrogen chloride was slowly evolved. The cooled melt was extracted with ether; a substance sensitive to moisture (probably tellurium tetrachloride) was then found to be present. The residue from the ether extraction, on crystallisation from boiling toluene, yielded 0·4 g. (or 33%) of the pure cyclic telluridichloride, identical with the following product in (2).

When the trichloride (5·6 g.) was heated at a lower temperature (150—160°) during 2 hours in a current of nitrogen, a lesser proportion of hydrogen chloride was evolved. On cooling, the melt solidified to a brown glass, which was powdered and dissolved in hot dry chloroform. The solution, kept out of contact with moist air, deposited pale pinkish-white micro-needles (0·5 g.) of a telluritrichloride (probably corresponding with formula VII) which, however, still contained traces of tellurium tetrachloride (Found: Cl, 27·3; whereas formula VII requires Cl, 26·4%). Recrystallised from hot benzene, the compound formed a voluminous mass of almost colourless, nacreous flakes, decomposing near 125° with darkening and evolution of hydrogen chloride. It was readily reduced by aqueous potassium metabisulphite to a red substance (probably the ditelluride), which was soluble in benzene but easily oxidised by the air, while in solution, to a less soluble substance.

The main product of the above reaction was a glutinous mixture containing free tellurium tetrachloride.

(2) *Action of heat upon an equimolecular mixture of tellurium tetrachloride and diphenyl ether.* Six experiments under varying condi-

tions were carried out, but the yield of cyclic dichloride seemed almost constant (about 50%). The following is a typical experiment: Tellurium tetrachloride (11.1 g.) and diphenyl ether (7.0 g.) were heated together in a flask with a long air-condenser, carrying a moisture guard-tube, a slow current of nitrogen being bubbled through the melt (this was not essential, however). The temperature was raised slowly from 100° to 240° over a period of 13 hours, when hydrogen chloride was evolved, mainly during two maximal phases, the first occurring near 120° and the second near 200°. The melt gradually thickened and after about 8 hours partly solidified even at 190°, but remelted as the temperature rose. The cooled melt finally set to a crystalline cake, which was ground to a loose brown powder. The powder was stirred with ether, filtered off, dissolved in acetone, and filtered from 0.8 g. of free tellurium. Evaporation of the acetone left 9.4 g. of the fairly pure cyclic dichloride (62%); but, on further purification of the product in a Soxhlet apparatus with toluene, the yield fell to 48%.

Keeping the temperature below 220°, reducing the time of heating to 5 hours, adding a little chloroform at the commencement of heating, and other similar modifications produced no important variation in the yield.

The material obtained by evaporating the ethereal extracts of the product contained free diphenyl ether or chlorinated diphenyl ether, as well as soluble tellurium compounds which could not be isolated from the viscous residues.

10 : 10-Dichlorophenoxtellurine (III) crystallises from boiling toluene in colourless, nacreous platelets, which melt without decomposition at 265° to a transparent, yellow liquid. At 100° the crystalline solid is yellow, but reverts to the colourless form on cooling. It is extremely stable to heat and can be vaporised without undergoing much decomposition; is almost insoluble in ether or petroleum, sparingly soluble in chloroform or ethyl alcohol, rather more soluble in benzene or toluene, and easily soluble in acetone. It is slowly hydrolysed by boiling water, a white oxide resulting. Boiling aqueous potash detaches the tellurium atom and generates diphenyl ether. The solution in cold concentrated sulphuric acid is yellow (Found: C, 39.8; H, 2.2; Cl, 19.3.  $C_{12}H_8OCl_2Te$  requires C, 39.3; H, 2.2; Cl, 19.35%).

*Phenoxtellurine* (VI).—The powdered dichloride (4 g.) was reduced at 0° with 25 c.c. of water and 4.8 g. (2 mols.) of potassium metabisulphite, slowly added with stirring, when sulphur dioxide was evolved. The yellow product was ground beneath the liquid in a glass mortar during an hour to complete the reduction, and the solid was then filtered off, washed with water, and dried. The

yield (3.2 g.) was nearly theoretical. The product was recrystallised from light petroleum (b. p. 40—60°).

*Phenoxtellurine* separates from hot petroleum in long, spear-like needles and from the cold solvent in large, transparent prisms, both forms being lemon-yellow to orange in colour, melting without decomposition at 78—79°, and having a delicate floral odour. The compound is very stable to heat and can be vaporised unchanged. It is insoluble in water, but easily soluble in ethyl alcohol, ether, benzene, or carbon tetrachloride to yellow solutions. It dissolves in cold concentrated sulphuric acid to a deep purplish-red solution, and is stable towards hot concentrated hydrochloric acid or dilute aqueous caustic soda [Found: C, 48.7; H, 2.9; Te, 43.4; *M*, cryoscopic in benzene, 287 ( $c = 1.25$ ), 294 ( $c = 2.18$ ).  $C_{12}H_8OTe$  requires C, 48.7; H, 2.7; Te, 43.1%; *M*, 295.5].

Warm concentrated nitric acid does not immediately cause nuclear nitration of phenoxtellurine, but produces the 10:10-dinitrate, which forms colourless needles decomposing near 258°. Bromine and iodine in chloroform solution readily yield respectively the 10:10-dibromide, bright yellow spangles from chloroform or primrose-yellow prisms from toluene (decomposing at 290°), and the 10:10-di-iodide, red spangles (decomposing indefinitely, mainly near 270°).

*Action of Heat upon Mixtures of Tellurium Tetrachloride and Diphenyl Ether in Various Proportions.*—(1) When it was attempted to introduce two  $-TeCl_3$  groups into the molecule of diphenyl ether by using 2 mols. of tellurium tetrachloride to 1 mol. of the aromatic ether and heating at 120° during 6 hours, only the telluritrichloride was obtained, part of the tellurium tetrachloride remaining unaltered.

(2) Tellurium tetrachloride and 2 mols. of diphenyl ether, heated at 110° to 180° during 8 hours, yielded only a mixture of a trichloride and the cyclic dichloride.

(3) Tellurium tetrachloride (1 mol.) and diphenyl ether ( $3\frac{1}{2}$  mols.), heated at 110° to 210° during 16 hours, gave a yield of 42% of 10:10-dichlorophenoxtellurine, showing that the tendency towards formation of this cyclic dichloride is maintained even in presence of a large excess of diphenyl ether.

The author's thanks are due to Professor Morgan for his kind interest in the work and for his gift of certain research chemicals.

UNIVERSITY OF BIRMINGHAM,  
EDGEASTON.

[Received, August 22nd, 1925.]

XXXIV.—*The Quaternary Salts of Benzoxazoles.*

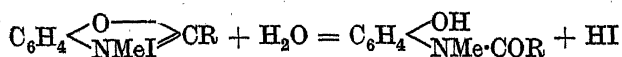
By LESLIE MARSHALL CLARK.

SINCE the pseudo-bases of the quaternary salts of substituted benzthiazoles have been shown to be *o*-acylmethylaminothiophenols (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2354; Clark, J., 1925, **127**, 973), the corresponding benzoxazole compounds have now been investigated so that a comparison may be made between the properties of these analogous ring systems.

Benzoxazole methiodide was first prepared by Fischer (*J. pr. Chem.*, 1906, **73**, 435), who showed that when the salt was heated with hydrochloric acid, *o*-methylaminophenol was formed, whilst treatment with hot alkalis caused profound decomposition.

It has now been found that benzoxazole methiodide, on being dissolved in water, gives a solution, acid to litmus, from which, after addition of one equivalent of caustic alkali, *o*-formylmethylaminophenol can be obtained. In the same way, 1-methylbenzoxazole methiodide\* and 1-phenylbenzoxazole methiodide readily hydrolyse in aqueous solution to *o*-acetylmethylaminophenol and *o*-benzoylmethylaminophenol, respectively, with the liberation of one equivalent of acid.

The reaction is therefore to be represented by the equation



No such effect is apparent in these quaternary salts as was observed by Skraup (*Annalen*, 1919, **419**, 80), who found that in the 1-substituted benzoxazole bases resistance of the oxazole ring to fission increases with increasing volume of the substituent radical.

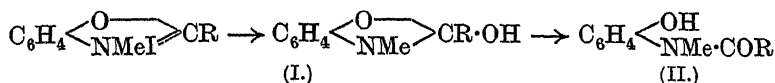
Attempts to reverse the hydrolysis were made by passing dry hydrogen iodide through a solution of *o*-benzoylmethylaminophenol in dry ether and by dissolving *o*-acetylmethylaminophenol in excess of concentrated perchloric acid. The hydriodide of the acylmethylaminophenol separated in the first case, but no 1-phenylbenzoxazole methiodide was obtained, and in the second the only substance isolated was the unchanged phenol.

There appeared to be some possibility that the complete scheme

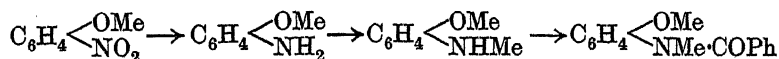
\* Since this paper was prepared for publication, König and Meier (*J. pr. Chem.*, 1925, **109**, 324) have shown that 1-methylbenzoxazole methiodide on hydrolysis with water gives *o*-acetylmethylaminophenol.



for the action of alkalis on substituted benzoxazole quaternary salts might be represented thus:



Were this the case, methylation might be expected to yield a derivative of each of the compounds I and II. On treating an aqueous solution of 1-phenylbenzoxazole methiodide with a slight excess of sodium hydroxide and methyl sulphate, only *o*-benzoylmethylaminoanisole could be isolated, whose identity was established by synthesis in the following stages:



Under these conditions, therefore, no evidence for the presence of the carbinol base (I) is obtained. Although there is thus a measure of similarity between benzoxazonium and benzthiazolonium salts in their reactions with alkalis, two important differences must be noticed:

(a) Benzoxazonium salts are hydrolysed by water alone, whereas benzthiazolonium salts are stable in aqueous solution.

(b) In consequence of this behaviour, benzoxazole quaternary salts cannot be obtained by treatment of the *o*-acylmethylaminophenols with acids, whereas benzthiazole methiodide is readily recovered from the sodium salt of formylmethylaminothiophenol (Mills, Clark, and Aeschlimann, *loc. cit.*).

## EXPERIMENTAL.

*Benzoxazole Methiodide.*—Benzoxazole was prepared by Ladenburg's method (*Ber.*, 1876, 9, 1924) by heating together *o*-aminophenol and formic acid. Fischer (*loc. cit.*) obtained the methiodide by heating the base with excess of methyl iodide at 100° for 3 hours, and describes it as yellow, shining needles, m. p. 182° (decomp.). In this investigation, the two substances were combined at temperatures varying from 50° to 100°; the product was similar in colour to Fischer's but melted at 202° (decomp.). The purest material was obtained by heating the base with 10% excess of methyl iodide at 60° for 8 hours and extracting the crushed product with dry ether (Found: C, 37.1, 37.25; H, 3.0, 3.1; N, 5.2; I, 48.8. Calc., C, 36.8; H, 3.1; N, 5.4; I, 48.6%).

*Action of Potassium Hydroxide on Benzoxazole Methiodide.*—From mixed aqueous solutions of the methiodide (10 g.) and potassium hydroxide (rather more than 1 equiv.), *o*-formylmethylaminophenol crystallised on cooling, and a further crop was

obtained by passing carbon dioxide through the mother-liquor. It crystallised from benzene in colourless needles (yield, 5 g.), m. p. 103—104° (Found: C, 63.6; H, 5.8; N, 9.0. Calc., C, 63.6; H, 6.0; N, 9.3%).

The *formyl* compound (1 g.) was heated for 1 hour with concentrated hydrochloric acid (7.5 c.c.) and water (4 c.c.), the solution made slightly alkaline with sodium hydroxide, and the alkali neutralised with carbon dioxide; 0.7 g. of almost colourless, shining flakes of *o*-methylaminophenol was obtained, m. p. 95—96° (Lees and Shedden, J., 1903, 83, 756, give m. p. 96—97° and Fischer, *loc. cit.*, gives m. p. 86—87°).

For further characterisation of the product, a nitroso-derivative was prepared by Dieppolder's method (*Ber.*, 1899, 32, 3519) from this compound, and from an authentic specimen of *o*-methylaminophenol. Both nitroso-derivatives and their mixture crystallised from alcohol in colourless, glistening plates, m. p. 125—126° (decomp.) (Found: N, 18.0. Calc., N, 18.4%).

*1-Methylbenzoxazole Methiodide.*—1-Methylbenzoxazole, prepared by Ladenburg's method (*Ber.*, 1876, 9, 1524), was heated (13.5 g.) with methyl iodide (17 g.) for 8 hours at 100°. The yellow mass was extracted with dry ether and crystallised from acetone in colourless needles, which became light brown unless rapidly dried; m. p. 196° (decomp.) (Found: C, 39.5; H, 3.6; I, 46.1. Calc., for  $C_9H_{10}ONI$ , C, 39.3; H, 3.6; I, 46.2%).

*1-Methylbenzoxazole Methopерchlorate.*—The methiodide was dissolved in a little cold water and treated with excess of a saturated solution of sodium perchlorate. A mass of colourless plates was immediately precipitated, m. p. 165—170°. Recrystallisation from water lowered the melting point to 150—160°, evidently causing decomposition. A portion of the crude perchlorate was extracted with ether, whereby the hydrolysis product, *o*-acetylmethylaminophenol, m. p. 150°, was removed. The purified *perchlorate* had m. p. 173°, unchanged by crystallisation from acetone-ether (Found: N, 6.0.  $C_9H_{10}O_5NCl$  requires N, 5.7%).

The salt (0.8 g.) was heated in aqueous solution for 1½ hours; colourless needles of *o*-acetylmethylaminophenol, m. p. 151°, crystallised on cooling (Found: N, 8.8. Calc., N, 8.5%).

1-Methylbenzoxazole methiodide in aqueous solution at laboratory temperature was hydrolysed incompletely after 8 hours and completely after 66 hours.

*Action of Potassium Hydroxide on 1-Methylbenzoxazole Methiodide.*—The reaction was carried out in the same way as for benzoxazole methiodide. The yield of *o*-acetylaminophenol, m. p. 151°, from 7 g. of salt was 2.1 g.

*Action of Silver Oxide on 1-Methylbenzoxazole Methiodide.*—The salt (1 g.) was dissolved in acetone (300 c.c.) and silver oxide freshly prepared from silver nitrate (3 g.) was added. Silver iodide was formed and after being shaken for 1 hour the acetone solution was evaporated: the residue was crystallised from benzene-light petroleum, colourless needles of *o*-acetylmethylaminophenol, m. p.  $151^{\circ}$ , being obtained.

*1-Phenylbenzoxazole Methiodide.*—1-Phenylbenzoxazole, prepared by Skraup's method (*loc. cit.*), was heated (3.8 g.) with methyl iodide (9 g.) at  $100^{\circ}$  for 36 hours. The product was extracted with dry ether and cautiously crystallised from absolute alcohol. The *methiodide* (yield 4.8 g.) separated in almost colourless needles, m. p.  $196^{\circ}$  (decomp.), which became brown on exposure to light (Found: C, 49.9; H, 3.6; I, 37.3.  $C_{14}H_{12}ONI$  requires C, 49.9; H, 3.6; I, 37.6%).

*Action of Water on 1-Phenylbenzoxazole Methiodide.*—When the salt (3.37 g.) was dissolved in warm water (100 c.c.), a colourless, crystalline substance immediately began to separate. The acid solution on titration with sodium hydroxide and phenolphthalein required 10.4 c.c. of *N*-NaOH (Calc. for 1 equiv. of NaOH, 10.0 c.c.).

The solid crystallised from aqueous alcohol in plates, m. p.  $163$ — $164^{\circ}$ , and was recognised as *o*-benzoylmethylaminophenol by analysis as well as by the method of preparation. Ransom (*Amer. Chem. J.*, 1900, 23, 34) gives m. p.  $162$ — $163^{\circ}$  (Found: C, 74.1; H, 5.6; N, 6.4. Calc., C, 74.0; H, 5.7; N, 6.2%).

The *urethane* was prepared by heating *o*-benzoylmethylaminophenol (1 g.) for 3 hours with phenylcarbimide (0.6 g.). The product was extracted with ether and crystallised from alcohol in colourless plates, m. p.  $144^{\circ}$  (Found: C, 73.3; H, 5.1; N, 8.2.  $C_{21}H_{18}O_3N_2$  requires C, 72.8; H, 5.2; N, 8.1%).

*o-Benzoylmethylaminoanisole.*—*o*-Methylaminoanisole, prepared by the usual reactions from *o*-nitroanisole, was benzoylated with benzoyl chloride and sodium hydroxide. The product crystallised from aqueous alcohol in small, colourless prisms, m. p.  $115^{\circ}$  (Found: C, 74.4; H, 6.1; N, 5.7.  $C_{15}H_{15}O_2N$  requires C, 74.7; H, 6.2; N, 5.8%).

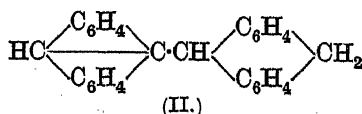
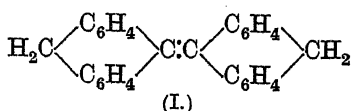
When 1-phenylbenzoxazole methiodide (1.5 g.) was shaken with sodium hydroxide and methyl sulphate in slight excess, a paste formed which was crystallised from aqueous alcohol. It melted at  $115^{\circ}$ , and did not depress the melting point of *o*-benzoylmethylaminoanisole prepared as described above (Found: N, 5.8%).

XXXV.—*Reactions of the meso-Hydroxyanthrones.*

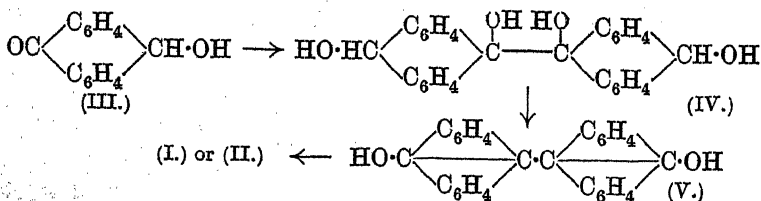
By MARCUS AURELIUS MATTHEWS.

THE reduction of 10-hydroxyanthrone\* by zinc dust and glacial acetic acid leads to anthrone, probably through addition of hydrogen to the carbonyl group and subsequent loss of water across the ring (K. H. Meyer, *Annalen*, 1911, 379, 37).

Anthrone itself on reduction with zinc and hydrochloric acid in glacial acetic acid undergoes the pinacol condensation (Barnett and Matthews, J., 1923, 123, 380), and it has now been found that under similar conditions 10-hydroxyanthrone also undergoes the pinacol condensation, although the reduction goes further and leads to *dihydrodianthranyl*, which may be (I) or (II) or a tautomeric mixture of these. The powerful blue fluorescence renders (II) the more probable, but the existence of fluorescence cannot be taken as definite proof of the presence of a "bridge" (compare Padova, *Ann. Chim.*, 1910, 19, 358, 435; Jüngermann, *Ber.*, 1905, 38, 2868).



The reduction of 10-hydroxyanthrone (III) to dihydrodianthranyl cannot take place through preliminary formation of anthrone, for, as already shown (Barnett and Matthews, *loc. cit.*), the reduction of this gives only dianthranyl and  $\alpha$ -anthrapinacolin. Further, neither dianthranyl nor dianthranol is attacked under the experimental conditions employed, although dianthranol is reduced to dihydrodianthranyl by tin and hydrochloric acid. It therefore follows that in the reduction of 10-hydroxyanthrone with zinc and hydrochloric acid attack first takes place at the carbonyl group, involving the formation of a pinacol (IV), and that further reduction of the pinacol must be due to ready attack of the "nascent" dianthranol molecule (V) formed by loss of water across the rings.



\* All the anthrone formulæ given in this paper are numbered with the carbonyl group in position 9.

10-Hydroxy-10-phenylanthrone differs from 10-hydroxyanthrone in giving on reduction a dianthranyl and not a dihydrodianthranyl derivative. Here the mechanism of the reaction probably consists in preliminary reduction to phenylanthrone, from which diphenyl-dianthranyl is very readily produced (Barnett and Cook, J., 1923, 123, 2631).

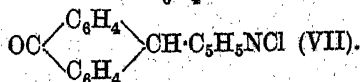
The zinc-hydrochloric acid reduction of the two  $\alpha$ -chloro-10-hydroxyanthrones gave compounds for which analytical figures corresponding to the  $\alpha$ -chloroanthrones were obtained. The compounds were not the  $\alpha$ -chloroanthrones, but each passed into the corresponding  $\alpha$ -chloroanthrone on treatment with alcoholic sodium hydroxide. These compounds are at present under investigation and their structure will be discussed in a future communication.

Further information on the mechanism of reduction of a hydroxyanthrone was obtained by comparing the behaviour of 10-hydroxyanthrone itself towards acids and towards reducing agents with that of the two  $\alpha$ -chloro-10-hydroxyanthrones:

	10-Hydroxy-anthrone gives	4-Chloro-10-hydroxyanthrone gives	1-Chloro-10-hydroxyanthrone gives
With HBr	10-Bromoanthrone	4-Chloro-10-bromoanthrone	1-Chloro-10-bromoanthrone
HCl	10-Chloroanthrone	4 : 10-Dichloroanthrone	1-Chloroanthraquinone and 1-chloroanthrone
HI (1 or 2 mols.)	Anthraquinone and anthrone	1-Chloroanthraquinone and 4-chloroanthrone	4 : 4'-Dichloro-9 : 9'-dianthrone, 1-chloroanthrone, and a trace of 1-chloroanthraquinone
Sn and HCl	Anthrone and a small amount of dihydrodianthranyl	4-Chloroanthrone	4 : 4'-Dichloro-9 : 9'-dianthrone
H <sub>2</sub> SO <sub>4</sub>	Anthraquinone and anthrone	1-Chloroanthraquinone and 4-chloroanthrone	1-Chloroanthraquinone and 1-chloroanthrone
Al and H <sub>2</sub> SO <sub>4</sub>	Anthrone	4-Chloroanthrone	1-Chloroanthrone.

10-Chloroanthrone is an extremely stable substance and is readily prepared in good yield by the direct chlorination of anthrone, although Goldmann (*Ber.*, 1887, 20, 2436; 1888, 21, 1176) failed to obtain it by this method. It is best identified in the form of

the *pyridinium* salt,  $\text{OH} \cdot \text{C} \begin{array}{c} \nearrow \text{C}_6\text{H}_4 \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{C} \cdot \text{C}_5\text{H}_5\text{NCl}$  (VI) or



The direct chlorination of 4-chloroanthrone gave 4 : 10-dichloro-

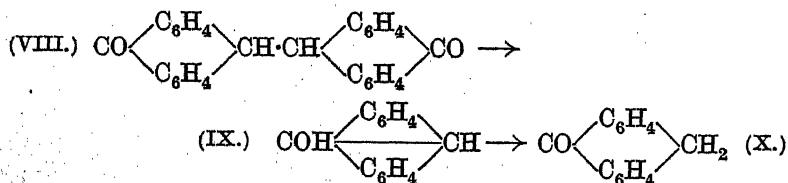
anthrone, whereas from 1-chloroanthrone the only product obtained was 4:4'-dichloro-9:9'-dianthrone, the 1:10-dichloroanthrone apparently being very unstable. It was not possible to prepare the last compound by the action of hydrogen chloride on the corresponding hydroxyanthrone, a disproportioning taking place with the production of the corresponding anthraquinone and anthrone. Other acids cause a disproportioning of the hydroxyanthrones, the mechanism of which has been discussed by Scholl (*Ber.*, 1923, 56, 1065).

Hydroxyanthrone is readily converted into anthraquinol by boiling water in absence of air, this being the best method for preparing anthraquinol.

Nitration of dihydrodianthranyl leads to a *nitrodihydrodianthranyl*, a reaction which favours formula (II) without, however, excluding formula (I). The nitration is not preceded by oxidation as in the case of dihydroanthracene (Meisenheimer, *Annalen*, 1902, 323, 205; 1904, 330, 133), or of dichlorodihydrodianthranyl (Barnett and Matthews, *J.*, 1923, 123, 2549), the product isolated in the latter case being dichlorodinitrodianthranyl.

Dihydrodianthranyl reacts slowly with excess of bromine in carbon disulphide solution with the production of *dibromodihydrodianthranyl*.

Dianthrane is converted by hydriodic acid in glacial acetic acid exclusively into anthrone and by tin and hydrochloric acid into a mixture of anthrone and dihydrodianthranyl. In these reactions it is improbable that anthrone is produced by the direct reduction of dianthrane and it seems almost certain that reduction is preceded by ketonisation to dianthrone, which is then reduced to anthrone. The suggestion was at first put forward (Barnett and Matthews, *J.*, 1923, 123, 380) that the reduction of dianthrone (VIII) to anthrone (X) was due to the instability of the dianthranyl ring system, reduction taking place at the bond joining the two *meso*-carbon atoms. Further work has rendered this view improbable, for if the single bond which joins the two anthracene ring systems in dianthrone shows this lack of stability, the corresponding double



bond in dianthraquinone should be even more susceptible to reduction. This, however, is not the case, dianthraquinone on reduction

giving dianthranol and not dianthrone. It therefore seems probable that hydrogen adds on to the carbonyl groups in dianthrone instead of to the single bond joining the two anthracene ring systems. In order to satisfy the requisite valencies, the "bridge" bond must be established with necessary rupture of the bond joining the two anthracene ring systems; the anthranol thus produced being at once ketonised to anthrone (X).

A similar explanation suffices to account for the reduction of 4:4'-dichloro-9:9'-dianthrone to the corresponding anthrone.

#### EXPERIMENTAL.

*Dihydrodianthranyl* (I or II).—To 20 g. of 10-hydroxyanthrone in 100 c.c. of boiling glacial acetic acid, 20 g. of zinc dust and 50 c.c. of concentrated hydrochloric acid were added simultaneously in small amounts. The addition of these two reagents must be simultaneous, since excess of hydrochloric acid causes decomposition of the hydroxyanthrone and excess of zinc dust brings about reduction to anthrone (Meyer, *loc. cit.*). After refluxing for 5 minutes the solid was separated from the hot solution. It crystallised from pyridine as an additive compound in greenish-yellow, flat needles, which lost pyridine on drying in the steam-oven for 3 days. The product (6 g.) became yellowish-grey and melted at 298–300° to a black liquid. In this state, it is pure enough for most purposes. For analysis it was recrystallised four times from benzene (Found: C, 94.5; H, 5.7.  $C_{28}H_{20}$  requires C, 94.4; H, 5.6%).

Dihydrodianthranyl exhibits an intense violet-blue fluorescence in organic solvents. It is easily soluble in chloroform, but less so in carbon disulphide, pyridine, acetone, or ether.

*Dibromodihydrodianthranyl*.—Excess of bromine (1 c.c.) was added to a cold solution of dihydrodianthranyl in carbon disulphide. After 12 hours, most of the carbon disulphide was distilled off, ether added, and the resulting solid recrystallised twice from small quantities of pyridine and dried in the steam-oven (Found: C, 65.4; H, 3.6; Br, 31.1.  $C_{28}H_{18}Br_2$  requires C, 65.4; H, 3.5; Br, 31.1%).

*Dibromodihydrodianthranyl* forms yellow crystals which do not melt at 320° and darken on exposure to light. Its solutions exhibit a blue fluorescence.

*Nitrodihydrodianthranyl*.—Excess of nitric acid (*d* 1.42; 2 c.c.) was added to 1.5 g. of finely powdered dihydrodianthranyl suspended in 50 c.c. of cold glacial acetic acid. After 12 hours, the solid was collected, washed with acetic acid, and dried in the steam-oven. The same compound was also obtained when the nitration was carried out at 80–100° and only one molecule of nitric acid

used. For analysis, it was recrystallised twice from glacial acetic acid, in which it was very sparingly soluble, separating in golden-yellow needles which melted and decomposed at  $305^{\circ}$  and darkened on exposure to light (Found: C, 83.6; H, 4.9.  $C_{28}H_{18}O_2N$  requires C, 83.8; H, 4.7%).

*Dichlorodinitrodianthranyl*.—Dichlorodihydrodianthranyl\* (Barnett and Matthews, J., 1923, 123, 2549) in cold glacial acetic acid suspension was resistant to nitric acid, but oxidation and nitration took place when 3 g. of the finely powdered material were suspended in 30 c.c. of glacial acetic acid, 2 c.c. of nitric acid ( $d$  1.42) added, and the whole slowly heated to the b. p. After cooling, the orange-red solid was collected, washed with acetic acid and ether, and recrystallised twice from small quantities of pyridine-alcohol. It then formed orange-red needles which became dark red on exposure to light and did not melt at  $330^{\circ}$  (Found: C, 65.5; H, 3.5; Cl, 13.8.  $C_{28}H_{14}O_4N_2Cl_2$  requires C, 65.5; H, 2.7; Cl, 13.8%).

*Reduction of 10-Hydroxy-10-phenylanthrone*.—To 2.3 g. of hydroxy-phenylanthrone and 25 c.c. of boiling glacial acetic acid, 2 g. of zinc dust and 4 c.c. of concentrated hydrochloric acid were added simultaneously, and the whole was boiled under reflux for 5 minutes. After cooling, the solid was collected and the excess of zinc removed by digestion with dilute hydrochloric acid. The resulting diphenyl-dianthranyl (1.5 g.) was identified by analysis (C, 94.9; H, 5.2. Calc., C, 94.9; H, 5.1%) and by direct comparison with an authentic sample.

*Reduction of Dianthranol*.—(a) To 3 g. of dianthranol and 5 g. of zinc dust in 40 c.c. of boiling glacial acetic acid, 8 c.c. of concentrated hydrochloric acid were added during  $2\frac{1}{2}$  hours, and the boiling was continued for a further  $\frac{1}{2}$  hour. The yellow solid which separated from the filtered solution on cooling consisted mainly of unchanged dianthranol.

(b) Finely powdered dianthranol (3 g.) and zinc dust (12 g.) were heated on the water-bath with 50 c.c. of ammonia ( $d$  0.880) and 50 c.c. of water for 3 days with occasional additions of more ammonia, sodium hydroxide, and zinc dust. The hot solution was filtered, the zinc dust extracted with dilute hydrochloric acid, and the residue recrystallised from pyridine; 0.6 g. of anthracene (m. p.  $217^{\circ}$ ) was thus obtained.

(c) Dianthranol (1 g.) was boiled under reflux for 5 minutes with 20 c.c. of glacial acetic acid and 2 c.c. (2 mols.) of hydriodic acid ( $d$  1.7), and the whole then diluted with hot water to incipient crystallisation. The dark crystals which separated on cooling were

\* The m. p. of this compound, owing to a misprint, was given in the paper cited as  $288^{\circ}$  instead of  $268^{\circ}$ .



boiled with potassium iodide solution, and 0.9 g. of anthrone obtained. Dianthrone under similar conditions also gave anthrone.

(d) Dianthranol (5 g.), tin (8 g.), and glacial acetic acid (80 c.c.) were boiled under reflux and concentrated hydrochloric acid (15 c.c.) was added during 1 hour. After boiling for a further  $\frac{1}{2}$  hour, the hot solution was filtered. The dihydrodianthranyl which separated on cooling was recrystallised from benzene (yield 0.8 g.). The acetic liquors on dilution with water gave anthrone, which was recrystallised from glacial acetic acid and converted into anthranyl acetate.

The products in (b), (c), and (d) were each identified by comparison with an authentic specimen.

*Reduction of Dianthraquinone.*—Dianthraquinone (0.5 g.) and zinc dust (2 g.) were suspended in boiling glacial acetic acid (10 c.c.), and concentrated hydrochloric acid (3 c.c.) was added during 20 minutes. After filtration, dilute hydrochloric acid was added and the solid recrystallised from acetone. It was identified as dianthranol by its complete solubility in cold aqueous sodium hydroxide and by the preparation of dianthranyl diacetate.

*1-Chloro-9-anthranyl Acetate.*—A mixture of 5 g. of 1-chloro-9-anthrone, 30 c.c. of pyridine, and 7 c.c. of acetic anhydride was heated on the boiling water-bath for 15 minutes and then poured into boiling water. The solid after recrystallisation from alcohol formed long, yellow needles, m. p. 110—112° (yield 4.8 g.). Its alcoholic solutions exhibit a blue fluorescence (Found: Cl, 13.2.  $C_{16}H_{11}O_2Cl$  requires Cl, 13.1%).

*4-Chloro-9-anthranyl Acetate.*—A similar mixture containing 4-chloro-9-anthrone\* was heated for 10 minutes, the subsequent procedure being as above. The product formed almost colourless needles, m. p. 124—126° (yield 4.6 g.) (Found: Cl, 13.2%). Its solution in alcohol had a blue fluorescence.

*1-Chloro-10-bromoanthrone.*—Bromine (4 c.c.; 1 mol.) was added to 18 g. of finely powdered 1-chloroanthrone suspended in 50 c.c. of carbon disulphide. The solid (22.5 g.), after being washed with carbon disulphide and ether, was pure enough for most purposes, but for analysis a sample was recrystallised twice from chloroform, in which it was moderately soluble, separating in faintly yellow crystals, m. p. 165° (decomp.), which darkened on exposure to light (Found: Cl + Br, 37.75.  $C_{14}H_8OClBr$  requires Cl + Br, 37.6%).

*1-Chloro-10-hydroxyanthrone.*—The above bromo-compound (22 g.) was boiled under reflux with 240 c.c. of acetone and 160 c.c. of water

\* In preparing this compound by Barnett and Matthews's method (*J.*, 1923, 123, 2549) the reduction must not be too prolonged, since it has been found that 4-chloro-9-anthrone—unlike anthrone itself—slowly undergoes the pinacol condensation with tin and hydrochloric acid with the production of dichlorodihydrodianthranyl.

until an almost clear solution was obtained (about 5 minutes), the filtered solution was cooled in ice, and 160 c.c. of water were added slowly.\* The resulting solid was recrystallised three times from benzene and then formed fine, white needles, m. p. 144—145°, which dissolved in boiling aqueous sodium hydroxide to form a deep red solution (Found: Cl, 14.6.  $C_{14}H_9O_2Cl$  requires Cl, 14.5%).

*4-Chloro-10-hydroxyanthrone*.—4-Chloro-10-bromoanthrone (5 g.) was refluxed with 120 c.c. of acetone and 80 c.c. of water for 15 minutes, the filtered solution cooled in ice, and cautiously diluted with 100 c.c. of water. The yellow solid (2.5 g.) was washed with water, dried in a vacuum desiccator, and twice recrystallised from benzene; it then formed faintly yellow crystals, m. p. 144—145°. It is not altered in m. p. by mixing with 1-chloro-10-hydroxyanthrone (Found: Cl, 14.5%).

*10-Chloroanthrone*.—(a) Dry hydrogen chloride was passed for 10 minutes through a suspension of 5 g. of finely powdered 10-hydroxyanthrone in 40 c.c. of toluene, a yellow precipitate forming. After dilution with light petroleum, the solid was collected and recrystallised from benzene, from which it separated with benzene of crystallisation, which was lost on drying in the steam-oven (Found: Cl, 15.5.  $C_{14}H_9OCl$  requires Cl, 15.5%).

*10-Chloroanthrone* forms colourless needles which melt and evolve gas at 225°. It is very much more stable than the corresponding bromo-compound and can be recrystallised from boiling xylene. It is stable towards boiling dilute solutions of alkali hydroxides, but dissolves in their alcoholic solution with a yellow colour. It is hydrolysed, but very much more slowly than 10-bromoanthrone, to 10-hydroxyanthrone by boiling with aqueous acetone.

(b) Finely powdered 10-hydroxyanthrone (1 g.) was boiled with 50 c.c. of concentrated hydrochloric acid for  $\frac{1}{2}$  hour. The product was recrystallised from xylene and identified by its conversion into anthronylpyridinium chloride (see below).

(c) Very finely powdered anthrone (40 g.) was added to 180 c.c. of a solution of chlorine in carbon tetrachloride (9.5% weight-volume). The reaction was extremely sluggish, but took place rapidly with evolution of heat on the addition of a trace of iodine, so that cooling with water became necessary. When it was complete (about 10 minutes) the whole was cooled in ice, and the solid, after being washed with carbon tetrachloride and ether, was dried in the steam-oven. The yield was 33 g. and the product pure enough for most purposes without further treatment. It was identified by its conversion into anthronylpyridinium chloride.

In this and the succeeding preparation the addition of water must be made cautiously, otherwise the product separates as an oil.

10-Hydroxyanthranyl-9-pyridinium Chloride (VI) or Anthronyl-pyridinium Chloride (VII).—Chloroanthrone (2 g.) was heated with 15 c.c. of pyridine on the water-bath for 15 minutes, the crystals were washed with ether and then twice recrystallised from very dilute hydrochloric acid; orange-red needles, m. p.  $204^{\circ}$  (decomp.), were obtained (Found: Cl, 11.0.  $C_{19}H_{14}ONCl, H_2O$  requires Cl, 10.9%).

This chloride is easily identified by its reactions, which are similar to those of the corresponding bromide (Barnett, Cook, and Grainger, J., 1922, **121**, 2059).

4 : 10-Dichloroanthrone.—(a) Dry hydrogen chloride was passed for 10 minutes through 3 g. of finely powdered 4-chloro-10-hydroxyanthrone suspended in 20 c.c. of benzene; the solid slowly dissolved and crystals began to separate. After addition of light petroleum, these were collected and twice recrystallised from small quantities of chloroform and light petroleum, faintly yellow crystals being obtained, m. p.  $127-128^{\circ}$  (Found: Cl, 26.9.  $C_{14}H_8OCl_2$  requires Cl, 27.0%).

1-Chloro-10-hydroxyanthrone, when treated with hydrogen chloride under identical conditions, gave a mixture of 1-chloro-anthraquinone and 1-chloro-9-anthrone.

(b) A solution of chlorine in carbon tetrachloride (10 c.c.; 9.5% weight-volume) was added to finely powdered 4-chloro-9-anthrone (3 g.) suspended in 10 c.c. of carbon tetrachloride. No reaction took place until a crystal of iodine was added; hydrogen chloride was then slowly evolved and the solid dissolved. After concentration to small bulk, light petroleum was added and the solid recrystallised from a small quantity of chloroform-light petroleum. It was identified as 4 : 10-dichloroanthrone by the method of mixed melting points.

1-Chloro-9-anthrone, when treated under identical conditions, gave 4 : 4'-dichloro-9 : 9'-dianthrone as the sole product.

*Anthraquinol*.—Finely powdered 10-hydroxyanthrone (3 g.) was boiled with 100 c.c. of air-free water in an atmosphere of carbon dioxide for 20 minutes. The precipitate was identified as anthraquinol by its complete solubility in cold aqueous sodium hydroxide, by its facile oxidation to anthraquinone, and by the preparation of anthraquinyl diacetate. If the boiling with water is continued for a longer time, the product will be contaminated with some anthraquinone.

The action of acids and reducing agents on 10-hydroxyanthrone and on the two  $\alpha$ -chlorohydroxyanthrones, the results of which are given in the theoretical part of this paper, were carried out as follows :

*Hydrobromic acid.* The conditions were similar to those already described in the case of hydrochloric acid.

*Hydriodic acid.* The hydroxyanthrone (1 g.) was dissolved in boiling glacial acetic acid (10 c.c.), 1 or 2 mols. of hydriodic acid (*d* 1.7) were added, the whole was boiled for 1 minute in an atmosphere of carbon dioxide, and the solution then diluted with water.

*Tin and hydrochloric acid.* The hydroxyanthrone (1 g.), glacial acetic acid (10 c.c.), and tin (2 g.) were boiled under reflux, and concentrated hydrochloric acid (2 c.c.) was added during 5 minutes. The dianthrone or dihydrodianthranyl was filtered from the boiling solution. The filtrate on cooling deposited the anthrone.

*Sulphuric acid.* The hydroxyanthrone was dissolved in a small quantity of concentrated sulphuric acid in an atmosphere of carbon dioxide, kept in the cold for 15 minutes, and the product precipitated by pouring into ice-water.

*Aluminium and sulphuric acid.* The hydroxyanthrone (1 g.) was dissolved in concentrated sulphuric acid (11 c.c.), and aluminium powder (0.25 g.) added with cooling. A series of colour changes took place, the end of the reaction being determined by frothing and by the changing of the dark colour of the solution to light yellow or green (about  $\frac{3}{4}$  hour). The product was precipitated by pouring into ice-water and purified by recrystallisation.

The identification of the compounds formed in the above reactions was effected usually by means of direct comparison with authentic samples. 1-Chloro- and 4-chloro-9-anthrone were differentiated by the preparation of the respective anthranyl acetates. When an anthrone occurred together with an anthraquinone, separation was not practicable by means of fractional crystallisation. The anthraquinone was detected by the anthraquinol test. The anthrone was detected by dissolving some of the mixture in boiling alcoholic sodium hydroxide and adding a drop of chloroform: if anthrone is present, a green colour is produced (compare Padova, *Compt. rend.*, 1909, 148, 290); if 1-chloro-9-anthrone is present, a green colour will also develop; but if 4-chloro-9-anthrone is present, a dirty brown colour appears, thus affording a means of differentiating between 1- and 4-chloroanthrones. The most effective way of identifying 4:4'-dichloro-9:9'-dianthrone was by reducing 0.5 g. with tin (1 g.) in boiling glacial acetic acid (40 c.c.) and adding concentrated hydrochloric acid (3 c.c.) until all the solid matter had gone into solution (1½ hours). After filtration from the undissolved tin, water was added to incipient crystallisation, and the 1-chloro-9-anthrone thus obtained identified by direct comparison with an authentic sample.

*Summary.*

1. The reduction of 10-hydroxyanthrone and 10-hydroxy-10-phenylanthrone has been studied. Both compounds undergo the pinacol condensation with the production of dihydrodianthranyl and diphenyldianthranyl respectively.
2. The reduction of dianthranol under various conditions has been found to give anthracene, anthrone, and dihydrodianthranyl.
3. The mechanism of the reduction of a dianthrone to an anthrone has been discussed.
4. 10-Chloroanthrone, a substance of remarkable stability, has been prepared by the action of hydrochloric acid on 10-hydroxyanthrone and of chlorine on anthrone.
5. The action of acids and reducing agents on hydroxyanthrone and 1- and 4-chloro-10-hydroxy-9-anthrone has been examined. With some acids a disproportioning to the corresponding anthraquinone and anthrone takes place; reduction usually leads to the corresponding anthrone.
6. Hydroxyanthrone is easily enolised to anthraquinol by boiling water.

The author desires to express his thanks to the Department of Scientific and Industrial Research for a grant which enabled him to carry out this work.

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[Received, September 14th, 1925.]

## XXXVI.—*cycloHexanespirocyclohexane*.

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THERE is remarkable agreement between the relative ease of production of homologous alicyclic rings, the "formation numbers" calculated from the interatomic angle ( $115^\circ$ ) in saturated carbon chains (Ingold, J., 1921, 119, 305), and the heats of ring formation (Stohmann and Kleber, *J. pr. Chem.*, 1892, 45, 475). The effect of substitution (particularly substitution of a *gem*-grouping) on the ease of closure in any of the simple *cycloparaffins* is very pronounced, even in comparison with the difference, in ease of ring formation, between one member of the series and the next. If, therefore, the above agreement is fundamental and not fortuitous, the introduction of a substituent should cause an alteration in the heat of formation of a *cycloparaffin* ring comparable with the differences, in heat of formation, between successive ring homologues; indeed,

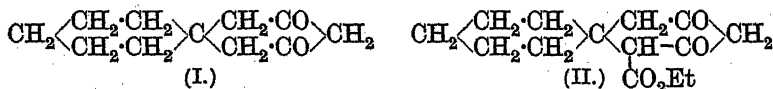
the alteration should be much greater than the accuracy of any individual determination. The application of thermochemical methods to the more complex cyclic substances encountered in the study of *spiro*-compounds and of condensed alicyclic systems should therefore be capable of giving an actual quantitative measure of the influence of substituents on ease of ring formation.

It would, for example, be possible, by determining the heats of combustion of two corresponding series of hydrocarbons (A) and (B), in which R and R' are progressively altered, to obtain a measure



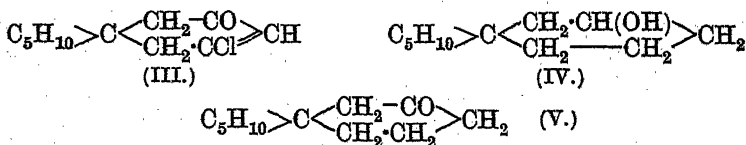
of the effect of substitution on the ease of closure of the ring present in (B). The chief interest of such a line of work would lie in the spirocyclic series. Spiran hydrocarbons have not, however, hitherto been described.\* One such hydrocarbon, *cyclohexanespirocyclohexane*, has now been prepared.

An account of the initial stages of the synthesis has already appeared (Norris and Thorpe, J., 1921, 119, 1199). *cyclohexanespirocyclohexane-3:5-dione* (I) was obtained by hydrolysing the ester (II); the latter was prepared by the condensation of Wallach's ketone, *cyclohexylideneacetone*,  $C_5H_{10} > C:CH \cdot COMe$ , with ethyl sodiomalonate. The reduction of the diketone (I) has now been



accomplished by indirect methods similar in general to those by which Crossley and Renouf (J., 1905, 87, 1494; 1907, 91, 63) prepared 1:1-dimethylcyclohexane.

Crossley and Le Sueur (J., 1903, 83, 110) found that dimethyldihydroresorcinol was converted into 5-chloro-1:1-dimethyl- $\Delta^4$ -cyclohexen-3-one by means of phosphorus trichloride in chloroform



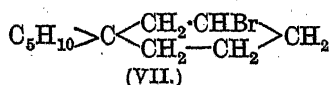
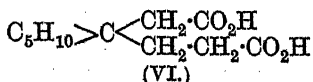
solution. The *spiro*-diketone (I) similarly gives the unsaturated *chloro-ketone* (III). Reduction of this with sodium and moist ether

\* Ingold (J., 1923, 123, 1706) has shown conclusively that the hydrocarbon hitherto represented to be *cyclopropanespirocyclopropane* consists essentially of *methylcyclobutene*, unaccompanied by any of its isomerides in the *cyclopropane* series.

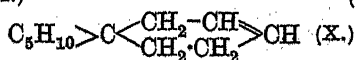
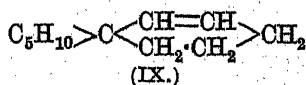
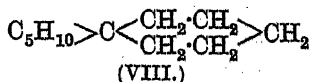
(compare Crossley and Renouf, *loc. cit.*) produced much resinous matter, from which only a trace of the *spiro*-alcohol (IV) could be isolated. However, by the action of zinc dust on the chloro-ketone in boiling glacial acetic acid solution, cyclohexanespirocyclohexan-3-one (V), which is analogous to Kon's cyclohexanespirocyclobutan-3-one (J., 1922, **121**, 515), was obtained in reasonable yield.

The refractive power of the ketone (V) was measured for sodium light and for the red and blue hydrogen lines, but not for the violet line on account of selective absorption. The molecular refraction shows inappreciable exaltation (0.08), in contrast with the increase (0.77) observed by Kon in the molecular refraction of his ketone; moreover, the molecular dispersion between the red and the blue shows no increase over the theoretical value. This result will not be surprising when it is remembered that *cyclopentanes* and *cyclohexanes* normally show scarcely any optical anomaly (compare Eisenlohr, "Spektrochemie organischer Verbindungen"), and that the figure of instability\* (maximum valency curvature) for cyclohexanespirocyclohexane is only 0.22, as against 0.18 for 1:1-dimethylcyclohexane, 0.08 for cyclohexane itself, and 0.13 for cyclopentane.

The ketone (V) gave, on reduction with sodium and moist ether, a good yield of cyclohexanespirocyclohexan-3-ol (IV). The constitution of this alcohol was confirmed by oxidising it with nitric acid to cyclohexane-1-acetic-1-propionic acid (VI).



The conversion of the *spiro*-alcohol (IV) into the *bromo*-derivative (VII) by the action of fuming hydrobromic acid presented unexpected difficulties. Not only did the replacement of the hydroxyl group by bromine proceed with great reluctance, but the boiling points of the two compounds lie very close together, rendering even partial separation a very tedious process. The same difficulty was encountered in attempts to isolate the corresponding *chloro*-derivative.



By reducing the impure bromo-compound (VII) in alcohol with zinc dust, cyclohexanespirocyclohexane (VIII) was obtained together

\* The figure of instability for a 6-carbon ring is expressed by

$$[\delta a / \delta S]_{s=0} = \sin \theta - \sqrt{3} \cdot \cos \theta.$$

with an unsaturated hydrocarbon (IX or X), evidently produced by loss of hydrogen bromide; a result contrasting with the production under similar conditions of 1:1-dimethylcyclohexane only from 3-bromo-1:1-dimethylcyclohexane (Crossley and Renouf, *loc. cit.*).

The final stage in the reduction was effected by shaking the mixture of saturated and unsaturated hydrocarbons with colloidal palladium in an atmosphere of hydrogen.

This investigation cannot be continued for the present, but it will, it is hoped, be concluded at some future date.

#### EXPERIMENTAL.

*cyclohexanespirocyclohexan-3:5-dione* (I).—The diketone of Norris and Thorpe (*loc. cit.*) has been further characterised by the formation, on hydrolytic fission, of *cyclohexane-1-acetone-1-acetic acid*,  $C_5H_{10}>C<\begin{smallmatrix} CH_2\cdot COMe \\ CH_2\cdot CO_2H \end{smallmatrix}$ . The diketone (1 g.) and 6 g. of crystalline barium hydroxide dissolved in 25 c.c. of water were heated at 200° for 24 hours. The ethereal extract of the acidified liquid left, after evaporation of the solvent, a pale yellow oil (yield practically quantitative), which set on cooling to a white solid and gave no colour with ferric chloride. The *keto-acid*, which is volatile in steam, is very soluble in ether, benzene, or alcohol, less so in water, or light petroleum (b. p. 40–60°); it separates from the latter in short, colourless needles, m. p. 67° (Found: C, 66.8; H, 8.8.  $C_{11}H_{18}O_3$  requires C, 66.7; H, 9.1%). The *semicarbazone* separates from methyl alcohol in colourless plates, m. p. 183.5° (decomp.) (Found: C, 56.55; H, 8.4; N, 16.6.  $C_{12}H_{21}ON_3$  requires C, 56.4; H, 8.3; N, 16.5%).

*Action of Phosphorus Trichloride on the Diketone* (I). *cyclohexanespiro-5-chloro-Δ<sup>4</sup>-cyclohexen-3-one* (III).—A mixture of 67 g. of the diketone (which must be dry and free from resinous matter and hydrochloric acid), 250 c.c. of dry chloroform, and 17.5 g. of phosphorus trichloride was heated under reflux for 3 hours, cooled, and the unchanged diketone filtered off. The residue after distillation of the chloroform was dissolved in a little ether and poured into 1300 c.c. of water, which was then extracted with ether four times. The ethereal solution, after being thoroughly washed with 10% sodium hydroxide solution (from which more of the diketone was obtained on acidification), was washed once with 25% sulphuric acid, twice with water, and dried over calcium chloride. The residue, after the ether had been removed through a column, was distilled under reduced pressure. The *chloro-ketone*, b. p. 167°/30 mm., 160°/17 mm., 157°/12 mm., solidified, on cooling, to a white, crystalline mass, which had a pungent camphor-like odour and



separated from light petroleum (b. p. 60—80°) in large, colourless prisms, m. p. 47° (Found : Cl, 17.8.  $C_{11}H_{15}OCl$  requires Cl, 17.8%).

The *semicarbazone* separates from methyl alcohol in glistening plates, m. p. 219° (decomp.) (Found : N, 17.0, 16.2.  $C_{12}H_{18}ON_3Cl$  requires N, 16.4%).

The recovered diketone (24%) was purified with difficulty, owing to the presence of resinous phosphorus compounds, and in many cases could not be used again.

*Reduction of the Chloro-ketone with Zinc Dust in Glacial Acetic Acid.* *cyclohexanespirocyclohexan-3-one* (V).—Zinc dust (33 g.) was added, the first portions in very small quantities because of the violence of the reaction, during 24 hours to a solution of 25 g. of the chloro-ketone in 80 c.c. of glacial acetic acid, boiling under reflux. The liquid was neutralised with caustic soda solution and steam-distilled. From the distillate, ether extracted the ketone (yield 86%).

The *semicarbazone* separated from ethyl alcohol in colourless, flattened needles, m. p. 224.5° (decomp.) (Found : N, 18.9.  $C_{12}H_{21}ON_3$  requires N, 18.8%).

The *ketone*, regenerated from the *semicarbazone* by boiling with oxalic acid and water in a current of steam, and extracted from the distillate with ether, was a colourless, mobile liquid, b. p. 225°/772 mm. or 130°/15 mm., having a pungent odour similar to that of cedarwood oil (Found : C, 79.8; H, 10.7.  $C_{11}H_{18}O$  requires C, 79.5; H, 10.9%). The freshly distilled ketone had  $d_{20}^{25}$  0.98417,  $n_D^{20}$  1.48432,  $n_D^{25}$  1.48685,  $n_F^{25}$  1.49322 (no violet light was transmitted). Hence  $[R_L]_D = 48.55$ ;  $[R_L]_{F-C} = 0.76$ , the calculated values being 48.61 and 0.75, respectively.

The ketone is stable towards neutral permanganate, and slowly attacked by the alkaline reagent in the cold.

The *oxime*, prepared by boiling the ketone for 1 hour with hydroxylamine hydrate (1.5 mols.) in aqueous-alcoholic solution, separated from light petroleum (b. p. 40—80°) in large, colourless prisms, m. p. 128° (Found : C, 73.1; H, 10.6.  $C_{11}H_{19}ON$  requires C, 72.9; H, 10.6%).

*Reduction of the spiroKetone with Sodium in Moist Ether.* *cyclohexanespirocyclohexan-3-ol* (IV).—A solution of 18 g. of the crude ketone (from the reduction of 25 g. of chloro-ketone) in 100 c.c. of ether and 10 c.c. of alcohol was poured on to 200 c.c. of water in a separating funnel, to which was attached a reflux condenser. Sodium (19 g., in thin slices) was gradually added, the water being changed after addition of the first 10 g.; this water was extracted with a little ether, which was then transferred to the funnel. When all the sodium had been added, the ethereal solution was washed

twice with water, the ether removed through a column, and the residue distilled in steam. The ethereal extract of the distillate was washed twice with a saturated solution of sodium bisulphite, and the ether distilled through a column; the residue solidified on cooling in a vacuum (yield 50% of the theoretical, calculated on the chloro-ketone used).

*cycloHexanespirocyclohexan-3-ol* boils at 127—128°/15 mm. and sets to a felted mass of needles, which are too soluble in the ordinary solvents to be recrystallised, but melt quite sharply at 58° after draining well on porous porcelain (Found: C, 78.5; H, 11.75.  $C_{11}H_{20}O$  requires C, 78.5; H, 12.0%). The alcohol has a pleasant camphoraceous odour.

The *p*-nitrobenzoate is produced when the hydroxy-compound and *p*-nitrobenzoyl chloride are boiled with pyridine in ethereal solution. It separates from alcohol in pearly-white plates, m. p. 102° (Found: C, 68.3; H, 7.25.  $C_{18}H_{23}O_4N$  requires C, 68.1; H, 7.3%).

*Oxidation of the spiroAlcohol.* *cycloHexane-1-acetic-1-propionic Acid* (VI).—The hydroxy-compound (19 g.) was gradually added to 45 c.c. of boiling, concentrated nitric acid, and the liquid was then diluted with water and evaporated. This process was repeated until no more nitric acid remained. A gummy acid (19.5 g.) was thus obtained (compare Crossley and Renouf, *loc. cit.*) which did not solidify. This was kept for 36 hours with 60 c.c. of absolute alcohol and 20 c.c. of concentrated sulphuric acid. The fraction, b. p. 179—183°/14 mm., of the neutral ester thus produced (Found: C, 66.4; H, 9.5.  $C_{15}H_{26}O_4$  requires C, 66.6; H, 9.7%) was hydrolysed with boiling alcoholic caustic potash, and the acid extracted from the acidified solution with ether. The residue left after evaporation of the ether gradually solidified when kept in a vacuum, and, after remaining for 3 days in contact with porous porcelain, was recrystallised from a mixture of chloroform and light petroleum (b. p. 40—60°), from which it separated in rosettes of colourless needles, m. p. 142.5° (Found: C, 61.45; H, 8.4.  $C_{11}H_{18}O_4$  requires C, 61.7; H, 8.4%).

The acid may also be purified through the characteristic *calcium* salt, the solubility of which in water apparently increases with increasing temperature almost to the boiling point, and then suddenly decreases.

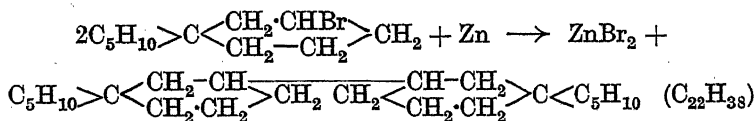
*Action of Hydrobromic Acid on the Hydroxy-compound.*—The *spiro*-alcohol (20 g.) was heated for 1.5 hours in a sealed soda-water bottle with 110 c.c. of fuming hydrobromic acid, saturated at 0°. The cooled liquid was resaturated with hydrogen bromide, and the

heating repeated. The product was poured into 1500 c.c. of water, and the heavy oil extracted with ether. The ethereal solution was washed well with a solution of sodium carbonate and then with water, and dried over calcium chloride. The residue, after the ether had been removed through a column, was distilled under reduced pressure. The greater portion boiled between  $133^{\circ}$  and  $136^{\circ}/12$  mm., but the liquid could not be separated into definite fractions, even by repeated distillation. A portion taken at  $133^{\circ}$  gave the following figures on analysis : C, 61.2; H, 8.7; Br, 29.2.  $C_{11}H_{19}Br$  requires C, 57.1; H, 8.3; Br, 34.6%. These correspond to 84% of the bromo-derivative, if only bromo-compound and hydroxy-compound were present. A purer sample was not obtained.

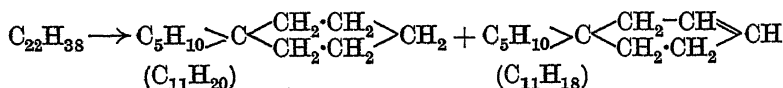
*Action of Hydrochloric Acid on the Hydroxy-compound.*—The reaction was conducted as in the preceding case. The fraction of the product most rich in chlorine boiled at  $142$ — $148^{\circ}/33$  mm. and contained 13.7% of chlorine, corresponding with the presence of 72% of  $C_{11}H_{19}Cl$  in the mixture. No fraction containing more than this amount of chlorine could be isolated.

*Reduction of the Bromo-derivative (VII) with Zinc Dust and Alcohol.*—The crude bromo-compound (26.5 g.), containing 84% of the pure material, was dissolved in 90 c.c. of 90% alcohol and mixed with 46 g. of zinc dust and an equal bulk of sand. Enough absolute alcohol (ca. 10 c.c.) was added to form a clear solution, and the whole heated under reflux on the water-bath for 20 hours. The liquid was filtered into 1200 c.c. of water, and the aqueous liquid extracted twice with ether. The ethereal solution was washed with water, and dried over potassium carbonate, the ether removed, and the residue heated for 2 hours over metallic sodium and then distilled. After two further distillations over sodium (the third time the metal remained unattacked), a bright, colourless liquid, b. p.  $204$ — $208^{\circ}/762$  mm., was obtained having a penetrating odour of geranium (Found in a fraction, b. p.  $204$ — $206^{\circ}$ : C, 87.4; H, 13.0. Found in a fraction, b. p.  $206$ — $208^{\circ}$ : C, 87.35; H, 12.9.  $C_{11}H_{20}$  requires C, 86.8; H, 13.2%.  $C_{11}H_{18}$  requires C, 88.0; H, 12.0%. A 50% mixture of  $C_{11}H_{20}$  and  $C_{11}H_{18}$  requires C, 87.4; H, 12.6%).

These figures indicate that the hydrocarbon contained some unsaturated material, a conclusion which was confirmed by the ready absorption of bromine in chloroform solution and by the reduction of permanganate in acetone solution. The analytical figures are so close to those given above for a 50% mixture that at first it was thought that a reaction in the following sense must have occurred :



followed by isomeric change on distillation :

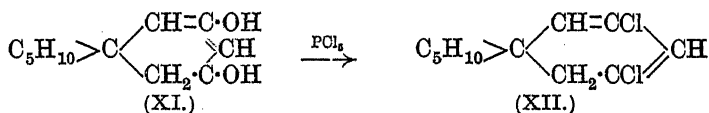


These figures have, however, never been repeated; moreover, 3 g. of the hydrocarbon mixture absorbed, in chloroform solution, 0.345 g. of bromine only, whereas for a 50% mixture 0.530 g. should have been taken up. It is concluded, therefore, that the remarkable agreement of the analytical results with the numbers required for the composition " $\text{C}_{22}\text{H}_{38}$ " is accidental, and that reduction and elimination of hydrogen bromide must have occurred simultaneously.

*Reduction of the Hydrocarbon Mixture with Hydrogen and Colloidal Palladium.* *cyclohexanespirocyclohexane* (VIII).—The mixed hydrocarbons (6 g.) were shaken in an atmosphere of hydrogen for 8 hours with 2.5 c.c. of a 10% solution of palladium chloride, 2.5 c.c. of a 10% solution of gum arabic in water, 5 c.c. of water, and enough alcohol to give a clear solution. The initial pressure of gas was 1070 mm.; this fell gradually to 815 mm. The product was isolated by distillation in steam and extraction of the distillate with ether.

*cyclohexanespirocyclohexane*, b. p.  $208^\circ/777$  mm., is a clear, colourless, mobile liquid having a faint odour of geranium (Found : C, 86.7; H, 13.35.  $\text{C}_{11}\text{H}_{20}$  requires C, 86.6; H, 13.3%). It is quite stable to permanganate and is only slowly dissolved by boiling, fuming nitric acid; bromine, in chloroform solution, is quite without action. The freshly distilled hydrocarbon has  $d_{20}^{25}$  0.87833,  $n_D$  1.47048,  $n_D$  1.47313,  $n_F$  1.47902,  $n_G$  1.48398. Hence  $[\text{R}_L]_D = 48.61$ ,  $[\text{R}_L]_{F-C} = 0.75$ ,  $[\text{R}_L]_{G-C} = 1.19$ . The theoretical figures are 48.60, 0.74, 1.19, respectively. These values show no optical exaltation such as might be expected were the *cyclohexane* rings in the *spiro*-hydrocarbon under a strain comparable with that in derivatives of *cyclobutane*, *cyclopropane* or *cycloheptane*. Crossley and Renouf (*loc. cit.*) quote the following results, determined for 1:1-dimethylcyclohexane by W. H. Perkin, sen.:— $d_{20}^{25}$  0.78543,  $n_D$  1.42958,  $n_D$  1.43728,  $n_G$  1.44203. Hence  $[\text{R}_L]_C = 36.85$ ,  $[\text{R}_L]_G = 37.78$ ,  $[\text{R}_L]_{G-C} = 0.93$ . The calculated figures are 36.78, 37.68, 0.90, respectively. The increase shown by the experimental figures over the theoretical is inappreciable.

*Action of Phosphorus Pentachloride on the spiro-Diketone (I). cycloHexanespiro-3 : 5-dichloro- $\Delta^{2:4}$ -cyclohexadiene.*—After it had been found that the conversion of the *spiro*-alcohol into the corresponding halogen derivatives could not be carried out quantitatively, it was hoped that an increased yield of the final product might be obtained by eliminating both oxygen atoms from the molecule at an early stage of the reduction. Accordingly the action of phosphorus pentachloride on the diketone was investigated, in the hope that the latter might react in the dienol form (XI) to give the dichloro-unsaturated hydrocarbon (XII); an expectation which has been realised.



The diketone (50 g.) was suspended in 130 c.c. of dry chloroform in a flask attached to a reflux apparatus; 125 g. of phosphorus pentachloride were gradually added in small quantities; after each addition the liquid boiled vigorously. The whole was heated for 3 hours on the water-bath, the cooled liquid filtered, and the chloroform distilled off. The residue was shaken well with ice-cold water, and the organic material taken up in ether. The ethereal solution, after being well washed with a dilute solution of caustic soda and then with water, was dried over calcium chloride. The residue after removal of the ether was distilled under reduced pressure. Only a very little impure diketone was recovered from the alkaline washings. *cycloHexanespiro-3 : 5-dichloro- $\Delta^{2:4}$ -cyclohexadiene* was thus obtained (yield 65%) as a pale yellow oil, b. p.  $152^\circ/21$  mm. (Found: Cl, 32.5.  $\text{C}_{11}\text{H}_{14}\text{Cl}_2$  requires Cl, 32.7%).

Unfortunately it has not yet been possible, by the use either of acid or of alkaline reducing agents, to prepare from this material a pure compound free from halogen.

This work was carried out at the Imperial College of Science and Technology under the direction of Professor J. F. Thorpe, C.B.E., F.R.S., to whom the author is grateful for kind help and encouragement. His thanks are also due to the Department of Scientific and Industrial Research and to the Chemical Society for grants which have made this research possible.

## XXXVII. — *The Interaction between Copper and Sulphuric Acid.*

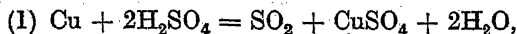
By CECIL WILLIAM ROGERS.

THE reactions which occur between copper and sulphuric acid have been investigated by Berzelius ("Traité de Chimie," IV, p. 324), Barruel (*J. Pharm.*, 1834, **20**, 13), Maumené (*Ann. Chim. Phys.*, 1846, **18**, 311), Calvert and Johnson (*J.*, 1866, **19**, 438), Pickering (*J.*, 1878, **33**, 122), Baskerville (*J. Amer. Chem. Soc.*, 1895, **17**, 904), van Deventer (*Chem. Centr.*, 1905, **1**, 992), and Sluiter (*ibid.*, p. 903).

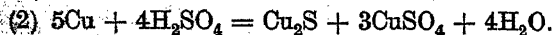
Berzelius noticed that a black residue formed during the reaction, which could be oxidised by nitric acid, and was of the opinion that it was the sub-sulphate. He made no analyses of the substance. Barruel found that the action could take place at the ordinary temperature if sufficient time was allowed. He held that sulphur dioxide was first formed which attacked the copper with the formation of cuprous sulphide and cupric oxide, the latter then dissolving in the excess of acid to form the sulphate. He also made no analyses of the supposed sub-sulphide. Maumené suggested that more than one reaction proceeds at the same time, and introduced the idea of two primary reactions with a number of secondary reactions. One of these primary reactions led to the formation of sulphur dioxide and cupric sulphate; the other to the production of cuprous sulphide as one resultant, which, in consequence of the secondary reactions, became oxidised through the stages  $\text{Cu}_2\text{S}$ ;  $\text{CuO}, 2\text{Cu}_2\text{S}$ ;  $\text{CuO}, 2\text{CuS}$ ;  $\text{CuO}, \text{CuS}$ ; to  $\text{CuO}$ . Calvert and Johnson carried out a few experiments on the relative effect of concentrated and dilute acid at temperatures between  $130^\circ$  and  $150^\circ$ . They observed the formation of cuprous sulphide, which they considered was due to free sulphur combining with the metal. They made no analyses, but gave the following reasons for their opinions: (1) No hydrogen sulphide is evolved, (2) no sulphur is volatilised, (3) the analogy between this reaction and that of sulphuric acid upon tin.

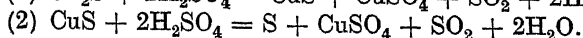
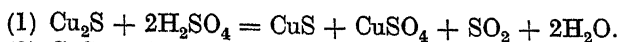
Pickering carried out a thorough examination of the subject in all its aspects and concluded that there were two primary reactions and two secondary reactions, the latter being dependent on the second primary reaction. He gave the following equations:

### A. *Primary Reactions.*



which was supposed to depend on the formation of nascent hydrogen.



*B. Secondary Reactions.*

He stated that the primary reactions may occur either alone or together; that the metal is attacked at all temperatures from 19° upwards, the extent of the action increasing with rise in temperature; that very little gas was observed below 130°, and none at all insoluble in water; and that a deposit of sulphur was formed in the neck of the vessel either before or after the complete dissolution of the metal. He showed that no hydrogen sulphide was evolved, and he was the first to point out that the black residue in the flask consisted solely of copper and sulphur in the proportions required by the formula  $\text{Cu}_2\text{S}$ . From his observation that the ratio of  $\text{Cu}_2\text{S}/\text{CuSO}_4$ , expressed in terms of the copper content, decreased with diminishing temperature, and that the maximum ratio obtainable in the case of the second primary reaction was 2 : 3, he attempted to ascertain the temperature at which this reaction should go on alone. In this he was not successful, although approximations were obtained with the concentrated acid at 80° and with dilute acid at 130°. In no case was a ratio greater than 2 : 3 observed. He gave a number of reasons to show that the sulphide could not be formed either by the action of nascent hydrogen, hydrogen sulphide, or by the direct action of free sulphur on the metal.

Baskerville also carried out a series of experiments in which most of his work was in accord with that of Pickering. He gave the same equations, but differed in the detail of the operation of the primary reactions. He held that the first primary reaction predominates at all temperatures between 0° and 270° and that the proportion of material conforming to the second primary reaction increases from 0° to 100°, and then decreases from 100° to 270°. Below 100°, the primary reactions alone take place, the secondary reactions becoming evident at the higher temperatures with prolonged action, although even then, with short time, evidence of the operation of only the primary reactions was found.

It is to be noticed that neither Pickering nor Baskerville took any account of the sulphur formed during the reactions beyond recording its formation and tracing its origin to the decomposition of the sulphides. They ignored altogether the possible influence it might have had on the results of their experiments, especially at the higher temperatures. Both are agreed that two primary reactions take place. The present work was undertaken to examine this question of two primary reactions, to discover reasons for the different views expressed upon their influence at various temper-

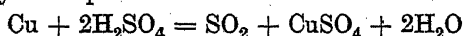
atures, and to ascertain the effect, if any, of the liberated sulphur upon the final result of the action.

#### EXPERIMENTAL.

The purest electrolytic copper foil obtainable and concentrated sulphuric acid (A.R.) were used. The foil was cut into pieces  $3 \times 1.6$  cm., one piece only being used in each experiment.

The apparatus consisted of a reaction tube, about 6 inches long, furnished with two tapped side tubes for the admission of an inert gas and the removal of the gaseous products, and a ground glass stopper from which the copper was suspended on a fine glass thread. Sufficient acid was employed to cover the metal completely when in the tube, the acid being maintained at the required temperature by means of a suitable bath for at least  $\frac{1}{2}$  hour before the introduction of the metal. A current of purified carbon dioxide was passed through the tube throughout an experiment, this creating an inert atmosphere, effectively removing the gaseous products, and keeping the surface of the metal fairly clean. The sulphur dioxide evolved, which was the only gaseous product of the reactions, was absorbed either by iodine or potassium permanganate. The amount of copper used was found by weighing the strip before and after an experiment, and the copper as sulphate was estimated as cupric oxide.

*The Completed Action.*—It is stated that at  $270^{\circ}$  the reaction represented by the equation



proceeds alone. A series of experiments carried out at  $270^{\circ}$  furnished evidence which, while supporting the above equation in so far as the final result is concerned, showed that this is not the only action which occurs. The complete conversion of the metal into the sulphate takes place within a few seconds of the introduction of the metal, and the gas is evolved with such rapidity that the copper is carried to the upper portion of the acid. Further, before the flood of gas commences, there is an appreciable interval, during which the surface of the metal becomes covered with a black deposit. This deposit is practically entirely acted upon at the conclusion of the experiment except for such very small particles as are carried out of the liquid by the upward rush of gas and deposited on the sides of the reaction vessel. The acid itself quickly assumes a blue colour and white crystals may be observed to fall continuously from the surface of the metal. The crystalline deposit at this temperature is always quite white and free from the grey tints found in that formed at lower temperatures. On examination under the microscope it is found to consist of a large number of imperfectly



formed crystals together with a few tabular crystals, the whole being characteristic of anhydrous copper sulphate when crystallised from the concentrated acid at the same temperature. The examination of the crystalline deposits obtained at different temperatures will be dealt with in a later section. The following results are typical of those obtained at this temperature :

No.	Cu used.	SO <sub>2</sub> found.	Cu as CuSO <sub>4</sub> .	Cu as sulphide.	Sulphur.	Acid.
1	0.2692	0.2618	—	Trace	Trace	Slightly brown
2	0.4649	0.4333	—	"	"	Brown
3	0.4450	0.4208	—	"	"	Slightly brown
4	0.4920	0.4841	0.4820	"	"	"
5	0.4929	0.5016	0.4631	"	"	Red
6	0.5012	0.5126	—	None	None	Colourless

The sulphur dioxide was estimated by absorption in iodine solution and titration of the excess iodine by thiosulphate. The low values for the copper sulphate are due to the fact that the anhydrous salt was filtered off before analysis, the 2—3% of copper which remained in solution thereby being left out of account. That copper still remains dissolved in the acid may be shown by the addition of a saturated solution of potassium bromide, when a dark, amorphous precipitate of the anhydrous bromide is thrown down. The excess of sulphur dioxide in experiments (5) and (6) is probably due to the dissociation of the acid itself; both experiments were prolonged for some time after the action had ceased. The lower values in some of the other cases are due to incomplete collection of the total sulphur dioxide owing to the closure of the experiments within a few seconds of the cessation of the reaction.

An interesting point arises in connexion with experiment (5). After the action had ceased, the reaction tube and its contents were allowed to cool slowly during several hours, and the acid liquid was then bright red. The crystalline deposit was quite normal when viewed under the microscope, and the abnormal colour may be ascribed, perhaps, to the colloidal condition of traces of sulphur remaining in solution. This suggestion is supported by the fact that after several weeks the acid deposited a small quantity of sulphur and became brown; the sulphur redissolved on shaking, producing a reddish-brown solution. All attempts to reproduce this effect met with failure.

Since traces of both sulphur and sulphide were met with at 270°, the reaction temperature was raised, but in the majority of cases both persisted. This circumstance, together with the darkening of the metallic surface before the evolution of gas commences, points to the conclusion that the simple equation is not sufficient to explain the action even at this high temperature, and that the

formation of sulphide and the subsequent liberation of sulphur are probably steps in the series of reactions involved.

*The Black Deposit.*—The black deposit was therefore carefully investigated. Trial experiments showed that it is produced most abundantly between 100° and 130°. The material for examination was prepared by immersing a large piece of the metal in the acid, a current of carbon dioxide being passed continuously. When the metal became coated, it was removed and at once plunged into thoroughly boiled water, beneath which the deposit was removed. The metal, after thorough cleansing and drying, was then returned to the acid, these operations being repeated until sufficient material had accumulated. Although the temperature range is most favourable to the rapid formation of the sulphidic matter, it also happens that the acid reacts with it fairly quickly, so that the actual amount of material collected is comparatively small. At lower temperatures, the rate of reaction is too slow for the rapid collection of the sulphidic matter.

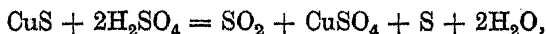
The deposit was transferred from the water to a small platinum funnel, thoroughly washed with boiled water, dried, and weighed. Any sulphur present was extracted with carbon disulphide. The material was then treated with hot, concentrated nitric acid until no further action took place, the residual sulphur being weighed. The sulphur was removed by ignition from the funnel, which was weighed once more as a check. The copper and the oxidised sulphur in the filtrate from the nitric acid treatment were then estimated as cupric oxide and barium sulphate, respectively.

A large number of analyses of this type were carried out, and in every case the total percentage of copper and sulphur was about 100. There can be little doubt that the black residue consists entirely of copper and sulphur. The ratio of copper to sulphur, however, varied considerably, even in specimens collected from the same piece of metal and the same acid for different analyses; but the proportions always exhibited values between those required for cuprous sulphide and cupric sulphide, being nearer to the former than to the latter. It appears, therefore, that the first product is cuprous sulphide, which is then decomposed partly into cupric sulphide. The following table shows results obtained by the method of analysis given above :

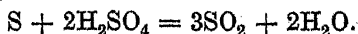
Temp.	Cu %.	S %.	Total %.
100°	78.72	21.49	100.21
110	75.44	25.32	100.76
110	77.43	22.11	99.54
120—125	72.54	30.36	103.20
125	73.77	25.67	99.44
132	78.29	21.56	99.85

$\text{Cu}_2\text{S}$  requires Cu, 79.86; S, 20.14% and  $\text{CuS}$  requires Cu, 66.48; S, 33.52%. No oxysulphides were obtained in any of these experiments.

*The Secondary Reactions.*—Experiments were then carried out with the two sulphides prepared by ordinary laboratory methods with the object of ascertaining the mode of decomposition of these substances in contact with the concentrated acid. Cupric sulphide was allowed to react with the acid at the required temperature until all had disappeared. The sulphur dioxide evolved was absorbed by iodine solution. A current of carbon dioxide was passed to assist in the removal of the sulphur dioxide, and to provide an inert atmosphere. The crystalline deposit was examined microscopically and found to be characteristic of cupric sulphate, and to contain inclusions of undecomposed sulphide. For the estimation of the copper, both the crystalline deposit and the acid liquid were taken, since some sulphate remained in solution. The sulphur dioxide evolved was, in general, in excess of that required by the equation given below, the excess increasing up to a definite maximum with rise in temperature and with the duration of the experiment. This can only have been due to the sulphur set free during the reaction, some of which reacted with the acid, while some was volatilised and condensed in pale yellow crystals of the  $\beta$ -form on the cooler parts of the reaction tube. The volatile material, on being heated on a microscope slide covered by a small glass dome, underwent all the changes characteristic of the effect of heat on sulphur. Small portions heated with free access of air gave the unmistakable odour of sulphur dioxide and reduced potassium dichromate. From the data given in the table below, it is evident that the cupric sulphide reacts with the acid according to the equation.



and that the sulphur reacts with more acid :



Temp.	CuS used.	CuO as $\text{CuSO}_4$ .	$\text{SO}_2$ found.
100°	1.486 g.	1.225 g.	1.152 g.
110	2.465	1.975	1.763
120	2.613	2.142	2.435
130	1.753	1.449	1.861
140	3.792	3.097	3.471
160	1.937	1.595	3.912 (prolonged action)
170	1.642	1.348	3.536     "     "

That cuprous sulphide reacts with sulphuric acid to produce cupric sulphide was established by the change of composition of the black sulphide after immersion in the acid for various periods, the acid being diluted considerably to stop the action. Sulphur

invariably made its appearance after a time. The experiments were made in pairs at different temperatures, one of each pair being stopped after a short time, the other carried on for some considerable time, especially at the lower temperatures, the rate of reaction being very slow. The original composition of the black sulphide was 79.81% Cu, 20.58% S in the two experiments at 60° and 79.82% Cu, 20.10% S in the others. The final compositions were :

Temp.	60°.	80°.	100°.	120°.	160°.
% Cu	75.71; 72.23	74.55; 69.64	76.82; 68.92	74.73; 68.51	76.22; 70.61
% S	24.18; 27.72	24.86; 30.02	22.81; 30.82	25.60; 30.72	23.51; 28.64

Sulphur dioxide was evolved continuously, but quantitative measurements were not made. Where a crystalline deposit was obtained, this was examined microscopically and found to be cupric sulphate. It thus appears that the cuprous sulphide decomposes into cupric sulphide with the simultaneous formation of cupric sulphate and sulphur dioxide according to the equation



and that the cupric sulphide so formed then reacts with the acid in the manner already described.

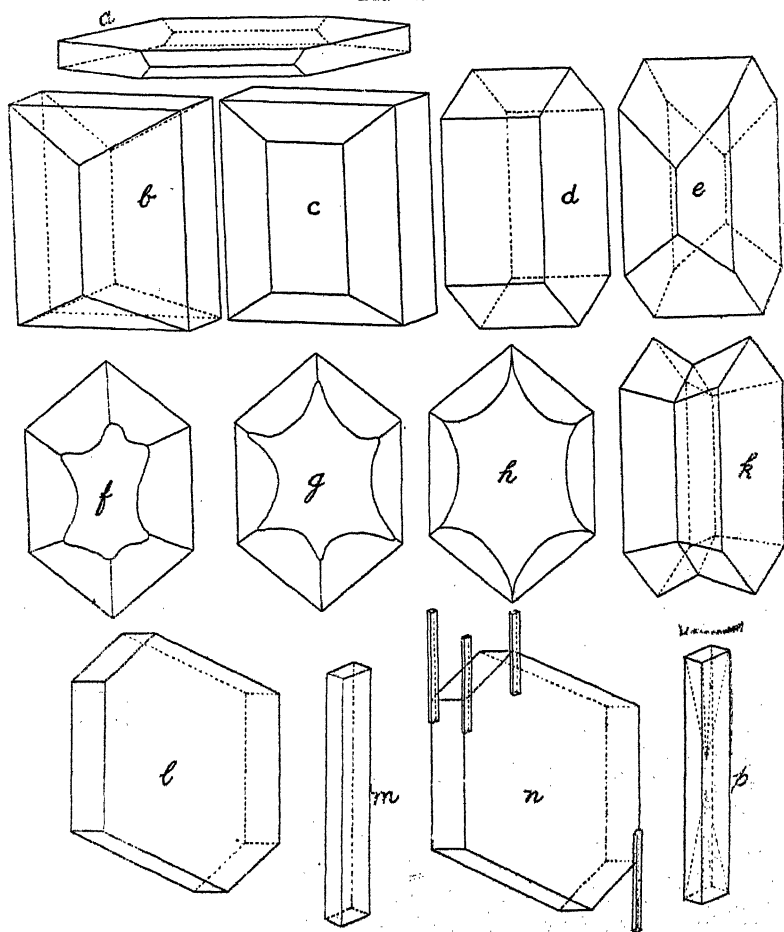
*The Crystalline Deposit.*—This has been stated by previous investigators to be anhydrous cupric sulphate, but as no means of identification were given, and owing to the possibility of the hydrolysis of a more complex substance on the addition of water, and the varying nature of some of the results obtained, it was thought necessary to examine the substance further. For this purpose the microscope was employed.

Except when prepared at the higher temperatures, above 200°, and even then, only when kept at this temperature for some time, under which conditions the substance is fairly soluble, producing a green solution, the deposit is never white; it is generally of a dingy grey appearance. This is due to the fact that it contains a quantity of the two sulphides, the particles of which have served as nuclei round which the crystals have formed, thus protecting them from further attack by the acid. If such a deposit be treated with acid at a temperature higher than that at which it was formed, some of the crystals will dissolve, and the sulphides thus liberated will react with the acid in the usual manner. The employment of sufficient acid to dissolve the whole of the deposit results in the formation of a perfectly white, sulphide-free product on cooling.

At temperatures up to about 200° the crystalline deposit consists almost entirely of crystals belonging to the rhombic system, being combinations of the pinacoids, prism, and macrodome. Typical crystals are shown in the diagram (types a, b, c, d, and e). These

are transparent and colourless, and frequently contain inclusions of sulphide. Twinning is not of common occurrence except in the case of type a. There are, in addition to these rhombic crystals, others which appear to be monoclinic, are green, grouped, few in number, and are formed chiefly at 130° and above, at which

FIG. 1.



temperature the solution also is green. They might possibly be the acid sulphate.

At temperatures above 200° deposits of an entirely different character are obtained. The crystals are, for the most part, imperfectly developed, and of the rhombic crystals, only those of type d reach full development. Types a, b, c, and e are absent. Various

intermediate stages in the growth of type d may be found in abundance, the earlier stages being represented by crystals with one fully developed hexagonal face, partial development of the corresponding parallel face, growth being greatest in the regions opposite to the angles of the hexagon, these faces being united by six inclined planes (types f, g, h). Continued growth of the irregular face leads ultimately to the formation of a hexagonal face corresponding to that originally present, the two being now united by twelve inclined planes and presenting the appearance of k. Subsequent growth fills up the hollows to produce the perfect crystal. The mode of formation appears to resemble that of the crystals of the alkali halides. In addition to these imperfect forms, there are a large number of monoclinic crystals, tabular parallel to the ortho axis (l). These are well developed. On cooling the solution obtained at these temperatures, no further deposition of rhombic crystals takes place; instead, long slender prisms make their appearance below about  $180^{\circ}$  (m). The prisms grow either on the monoclinic crystals just mentioned, or singly, or, occasionally, in groups. They appear to belong to the triclinic system, although their arrangement parallel to the orthopinacoid when growing on the monoclinic plates suggests that they also might be monoclinic (n). Many of them are hollowed out from the position of the basal pinacoid faces inwards, presenting the appearance of p. Copper sulphate pentahydrate, specially prepared for the purpose, was dehydrated either by heat, or by immersion in concentrated sulphuric acid for some days. The anhydrous substance, prepared in either manner, in solution in the concentrated acid below  $180^{\circ}$ , deposits nothing but the prismatic crystals previously mentioned. If, however, the solution is prepared at, say,  $160^{\circ}$ , so that it will become saturated at a considerably lower temperature, and is then set aside out of contact with moisture, nothing deposits from it for some time, but when crystallisation does set in, the rhombic crystals are formed to the exclusion of the long, slender prisms. This process may require two or more days for its completion.

At temperatures above  $200^{\circ}$  the crystals obtained showed all the characteristics of those prepared by the action of the acid on the metal. It was found, further, that neither carbon dioxide nor sulphur dioxide exerted any influence on the type of crystal developed at any temperature, and that no sulphur dioxide was evolved on heating the crystals with the acid. There can be little doubt, therefore, that the crystalline deposit obtained by heating the acid with the metal is anhydrous cupric sulphate; moreover, it appears that the anhydrous salt is at least dimorphous, and possibly tetramorphous.

*The Primary Reaction.*—Both Pickering and Baskerville were agreed that two primary reactions take place. It would seem rather unusual, however, for two substances to react in two totally different ways at the same temperature unless one of them be metameric. Of the reactants concerned, the acid is the only one which could fulfil this condition, and there is no evidence to show that it does actually exist in more than one form. Hence it is to be expected that only one primary reaction could take place. Further, both Pickering and Baskerville state that below  $130^{\circ}$  the evolution of gas is very slow, and that only at this temperature do bubbles of gas make their appearance. If the acid acted on the metal directly with the production of sulphur dioxide, it would be expected that bubbles of gas would be observable with ease at much lower temperatures, as in the case of zinc with dilute sulphuric acid. Even if the zinc and the acid be highly purified, the bubbles may be readily detected, although the action is slow. This again points to the possibility that the gas does not arise from the direct action of the acid on the metal, and that two primary reactions do not, in fact, take place.

If a piece of the purest electrolytic copper foil be totally immersed in the concentrated acid which has been heated to, and maintained at, a given temperature in an atmosphere of carbon dioxide for about  $\frac{1}{2}$  hour before the introduction of the metal, the following observations may be made :

*At  $50^{\circ}$ .* The first visible product of the interaction is a film on the metal, of a brownish hue, the formation of which is indicated by the loss of lustre of the metallic surface. This film gradually leaves the surface of the copper, the whole of which it covers, and it is then seen to be of almost the same shade as the metal itself. It remains suspended in the acid, being slowly moved about by the convection currents, and may be observed to change its colour to yellow and then to disappear—dissolve in the acid—colouring the latter yellow also. After this cycle of changes has proceeded for some time the acid becomes opalescent. No gas bubbles can be observed on the surface of the metal, yet sulphur dioxide is undoubtedly formed after a time.

*At  $50$ — $120^{\circ}$ .* On increasing the initial temperature the formation of the brown material takes place with increasing rapidity, as also the conversion of this into the yellow substance. No gas bubbles can yet be observed.

*At  $130$ — $140^{\circ}$ .* At about  $130^{\circ}$  the same phenomena occur with great rapidity, and at the same time bubbles of gas make their appearance; but no bubbles are formed until a deposition of the film has taken place. The particles constituting the film at this

temperature soon coalesce, the material then appearing black and forming a coating on the metal. The acid darkens owing to the suspended sulphide, but if the metal be removed it rapidly becomes clear again. Sulphur is deposited on the cooler parts of the apparatus.

The initial formation of the brown film could still be detected at temperatures above  $140^{\circ}$ . In every case there was an appreciable interval between the immersion of the metal and the appearance of the gas bubbles, which were never formed until the black sulphide had been produced. Hence the formation of sulphur dioxide is probably not due to the direct action between the acid and the metal. Support for this contention is found in the results of the following experiments.

A single piece of foil was totally immersed in the concentrated acid contained in one of the reaction tubes, the exit tube from which was connected by a series of T-pieces to absorption tubes in such a manner that any one of the latter could be put into communication with the reaction vessel directly, the change from one to another being made with the utmost facility. A current of carbon dioxide was passed throughout each experiment, the acid being heated to, and maintained at the required temperature for at least  $\frac{1}{2}$  hour before the introduction of the metal. The sulphur dioxide evolved was absorbed in potassium permanganate.

*Experiment 1.* At  $50^{\circ}$ . Twenty c.c. of  $N/50$ -potassium permanganate were placed in each of three absorption tubes, each being connected in turn to the reaction vessel. Upon the removal of each tube 25 c.c. of  $0.918 N/50$ -oxalic acid were added to its contents, and the volume of permanganate solution required for the titration of the excess of oxalic acid was measured. In all these experiments the reagents were delivered from over the same range of the burettes employed, this ensuring uniformity in the quantities of liquids taken. By blank tests it was found that 4.8 c.c. of the permanganate solution were required to titrate the excess of oxalic acid. The following results were obtained :

1.	Removed after the expt. had proceeded for	5 mins.	.....	4.8 c.c.
2.	" " " " " "	17 "	.....	4.7 "
3.	" " " " " "	30 "	.....	4.9 "

No film had yet formed.

*Experiment 2.* At  $60^{\circ}$ . The same piece of copper was employed with fresh acid, the remaining details conforming to those of Experiment 1.

1.	Removed after the expt. had proceeded for	5 mins.	.....	4.8 c.c.
2.	" " " " " "	19 "	.....	4.9 "



The film had formed and was about to leave the surface of the copper.

*Experiment 3.* At 50°. The same piece of copper was used with fresh acid.

- |   |          |
|---|----------|
| 1. Removed after the expt. had proceeded for 5 mins. .... | 4.8 c.c. |
| 2. " " " " " " 50 " .....                                 | 4.9 "    |

The film had just made its appearance.

- |  |          |
|--|----------|
| 3. Removed after the expt. had proceeded for 70 mins. .... | 4.9 c.c. |
| 4. " " " " " " 100 " .....                                 | 5.0 "    |

These experiments, and others carried out in a similar manner, clearly indicated that the sulphur dioxide is not produced before the formation of the sulphide, but that after the formation of the latter the liberation of the gas commences. The varying time interval between the immersion of the metal and the appearance of the film is probably due to the nature of the metallic surface.

In order to test the above experiments and to gain additional evidence, another series was carried out with the solutions of permanganate and oxalic acid diluted to  $N/200$ , so that the oxalic acid became  $0.918 N/200$ . The titrations were carried out in Nessler cylinders, the end-points being judged by comparison with similar cylinders containing known amounts of permanganate. By blank tests, it was found that 20 c.c. of permanganate with 25 c.c. of oxalic acid required 5.0 c.c. of permanganate to titrate the excess of oxalic acid.

*Experiment 1.* At 60°.

- |  |          |
|--|----------|
| 1. Removed after the acid had been heated for 45 minutes before the addition of the copper ..... | 5.0 c.c. |
| 2. Removed 10 minutes after the addition of the copper .....                                     | 4.9 "    |
| 3. " 36 " " " " " " " .....  | 5.2 "    |

Film formation first observed at this point.

- |   |        |
|---|--------|
| 4. Copper removed after 90 minutes' contact with the acid and the $KMnO_4$ allowed to absorb the $SO_2$ during a further 60 minutes at the same temperature ..... | 11.05, |
|---|--------|

*Experiment 2.* At 85°. Same piece of copper used with fresh acid.

- |  |          |
|--|----------|
| 1. Removed after the acid had been heated for 30 minutes before the addition of the copper ..... | 5.0 c.c. |
| 2. Removed 12 minutes after the addition of the copper .....                                     | 4.8 "    |
| 3. " 20 " " " " " " " .....  | 4.8 "    |

First indication of film formation.

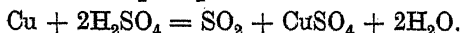
- |   |       |
|---|-------|
| 4. Copper removed after 45 minutes' immersion, the $KMnO_4$ being allowed to absorb the total $SO_2$ during a period of 2 days (30 c.c. of $KMnO_4$ and 20 c.c. of oxalic acid being used in this case) ..... | 7.2 " |
|---|-------|

These experiments again show that no sulphur dioxide is derived from the action before the film of sulphide has been formed, that no sulphur dioxide is derived from the acid itself at this temperature, and that the production of sulphur dioxide commences after the sulphide has formed.

There is, therefore, no justification for asserting that two primary reactions occur. For, if the first primary reaction of Pickering and Baskerville predominated at all temperatures, sulphur dioxide would be expected before the formation of the film, and if the second primary reaction took precedence, as asserted by Baskerville at the particular temperature of these experiments, no change should be observable in the sulphide film, and the gas evolved should first appear on the surface of the metal.

There is only one primary reaction, that one producing cuprous sulphide and cupric sulphate irrespective of the temperature at which the experiment is carried out, the sulphide then decomposing in the usual manner. The formation of the sulphur dioxide is thus dependent on the secondary reactions between the acid, the sulphides and the sulphur, the quantity actually formed being governed by the extent of occlusion of the sulphides by the sulphate, and the volatility of the sulphur in addition to the time and concentration factors.

The following experiments were made with the object of ascertaining the total production of sulphur dioxide at different temperatures, its amount being also expressed as a percentage of that theoretically obtainable from the simple equation



The experiments were prolonged until all the sulphides had disappeared, and the sulphur had either reacted, volatilised, or remained practically inactive, and all the sulphur dioxide had been collected :

Temp.	Cu used.	SO <sub>2</sub> found.	Per cent.	Temp.	Cu used.	SO <sub>2</sub> found.	Per cent.
50°	0.0013	0.0009	69	140°	0.2146	0.1853	86
50	0.0011	0.0006	55	180	0.3621	0.3317	91
85	0.0052	0.0025	50	200	0.3165	0.2849	90
100	0.0131	0.0075	57	270	0.4920	0.4841	98
110	0.0163	0.0124	76	270	0.4450	0.4208	95
120	0.0251	0.0213	85				

It is clear that the percentage of sulphur dioxide increases with increase of temperature. So also does the rate of reaction between the sulphides, the sulphur, and the acid, so that these substances have less chance of being occluded or volatilised. As the temperature increases, they are acted upon more and more rapidly until,

in the region of  $270^{\circ}$ , they are removed practically as fast as they are formed. It is also evident that below  $100^{\circ}$  the sulphur must react with the acid very slowly, in fact it is sometimes possible to find quite large particles present in the liquid after several days. If the quantity of acid employed be sufficiently large to dissolve the whole of the sulphate produced, thus preventing occlusion, and the time of the experiment be prolonged, there seems no reason, other than the volatility of the sulphur, why results closely agreeing with the simple equation should not be obtained at any temperature at which appreciable action between the substances concerned takes place. In particular, over the range  $130$ — $200^{\circ}$ , the sulphur is volatilised to an extent sufficient to allow its weight to be determined. The continuous removal of the sulphide makes impossible the direct determination of the quantitative relationships of the first reaction, but if an experiment be stopped at any point, and the cuprous sulphide and the sulphur dioxide be estimated, it is possible to obtain approximate values. From the consideration of the secondary reactions, it is known that 40% of the sulphur dioxide evolved in the completed reactions is due to the decomposition of the sulphides. If the corresponding amount of cuprous sulphide be calculated and this result be added to the sulphide actually found, the total must represent that portion of the copper which has either passed, or is passing through, the sulphide stage. The difference between this figure and the total copper used gives the amount of metal which would have been found as sulphate had no sulphide been decomposed. The ratio of copper as cuprous sulphide to copper as cupric sulphate then determines the action.

The following table shows the results of a number of experiments calculated in this manner :

Temp.	Cu used.	Cu as $\text{Cu}_2\text{S}$ .	$\text{SO}_2$ .	Cu as $\text{Cu}_2\text{S}$ = 40% of $\text{SO}_2$ .	Total Cu as $\text{Cu}_2\text{S}$ = A.	Residual Cu as $\text{CuSO}_4$ = B.	Ratio A/B.
$16^{\circ}$	0.1176	0.0113	0.0513	0.0205	0.0318	0.0858	2/5.4
80	0.0280	0.0013	0.0215	0.0086	0.0099	0.0181	2/3.7
80—90	0.0235	0.0005	0.0216	0.0086	0.0091	0.0144	2/3.2
100	0.0135	0.0016	0.0092	0.0037	0.0053	0.0082	2/3.1
100	0.0417	0.0120	0.0084	0.0034	0.0154	0.0263	2/3.4
120	0.0431	0.0085	0.0200	0.0080	0.0165	0.0266	2/3.2
140	0.0526	0.0079	0.0288	0.0115	0.0194	0.0332	2/3.4
160	0.2167	0.0217	0.1473	0.0589	0.0806	0.1361	2/3.4
170	0.2483	0.0198	0.1926	0.0771	0.0969	0.1514	2/3.1
190	0.2936	0.0176	0.2387	0.0995	0.1131	0.1805	2/3.2
200	0.3137	0.0157	0.2585	0.1034	0.1191	0.1946	2/3.3
240	0.4361	0.0087	0.3972	0.1589	0.1676	0.2685	2/3.2

Making allowance for the comparative inactivity of the sulphur at  $16^{\circ}$  and for the volatilisation of the sulphur at the higher temperatures, both of which tend to lower the ratio, it is clear that the value

of Cu as Cuprous Sulphide/Cu as Cupric Sulphate approximates to 2/3. This is satisfied by the following equation :



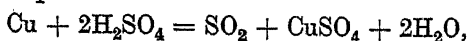
which is the second primary reaction of Pickering and Baskerville. If this equation be added to those given for the secondary reactions, the simple equation—the first primary of Pickering and Baskerville—is obtained.

It will now be evident why it was considered that one of the primary reactions proceeded alone at 270°. The various actions succeed one another so rapidly that there is little chance of any sulphide or sulphur escaping. Hence the quantity of sulphur dioxide evolved agrees closely with that required theoretically. Pickering's failure to determine the temperature at which his second primary reaction took place exclusively is also explained. It proceeds alone momentarily only, for as soon as a film of cuprous sulphide is formed it begins to react with the acid. The obstructive properties attributed to the compact deposit of sulphide on the surface of the metal are due not so much to the sulphide itself as to the layer of inert sulphate with which it soon becomes covered when the acid is saturated; for, if a further quantity of acid be added so as to reduce the concentration of the sulphate, and thereby allow some of that on the metal to dissolve, the action at once becomes vigorous again.

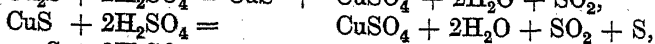
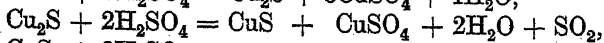
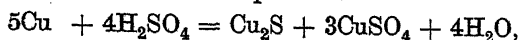
#### *Summary.*

It is shown by these experiments that :

1. There is only one primary reaction.
2. The sulphur produced exercises a considerable influence on the final results of the reaction, very much more than has been ascribed to it hitherto.
3. The white crystalline deposit is undoubtedly anhydrous cupric sulphate, and this substance is at least dimorphous.
4. At any temperature the completed reaction may be represented by the simple equation



which is the sum of the equations



these representing the actual sequence of events, and which, in suitable combination, will yield an equation expressing the stage attained by the reactants at any particular moment during an interaction.

In conclusion, the author desires to acknowledge his indebtedness to the Research Fund Committee of the Chemical Society for a grant and the loan of apparatus that enabled this research to be carried out.

THE GRAMMAR SCHOOL,  
MOOR PARK, PRESTON.

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### XXXVIII.—*Hydrogen Electrode Studies of the Reactions between Solutions of Salts of Weak Metallic Bases and the Acetate, Oxalate, and Tartrate of Sodium, with a Note on the Effect of Dextrose on Zirconium Chloride Solution.*

By HUBERT THOMAS STANLEY BRITTON.

It has been shown (this vol., p. 125) that in the reactions between certain metallic salts and the alkali-metal salts of very weak acids (chromic [second stage], boric, and carbonic), basic substances separate when the solutions attain the  $p_H$  at which the respective hydroxides are precipitated.

The present paper deals with the reactions of the sodium salts of moderately weak acids, weak at least in respect of one stage of ionisation, with solutions of salts of weak bases and of bases which form "soluble basic salts." Sodium tartrate was one of the salts selected, first because of the comparative weakness of the acid and secondly because it was thought that the titrations might give some insight into the nature of complex tartrate solutions. Titrations with the hydrogen electrode have also been made of zirconium chloride solutions containing dextrose and alkali, in order to study the function of the hydroxy-group in these complex solutions.

All the electrometric titrations now recorded were performed with the hydrogen and normal calomel electrodes described in J., 1924, 125, 1576; 1925, 127, 2111.

#### I. *Sodium Acetate Titrations.*

As acetic acid has a small dissociation constant,  $1.8 \times 10^{-5}$ , it was thought that the hydron concentrations produced during some reactions would be so low that the  $p_H$  would not be attained at which the hydroxides are precipitated, and it was expected, therefore, that basic acetates would be obtained from solutions of salts of the weakest bases.

*Zirconium.*—A solution of zirconium oxychloride,  $ZrOCl_2$ , slowly yields a precipitate on treatment with sodium acetate, but no pre-

cipitate is produced if there has been added to the solution the quantity of hydrochloric acid corresponding with the formula  $\text{ZrCl}_4$ .

The solubility of freshly precipitated zirconium hydroxide in acetic acid is inconsiderable; and this is in accord with hydrogen-ion requirements, for zirconia is precipitated from chloride or sulphate solution (J., 1925, 127, 2135, 2138) before the hydron concentration has been reduced to  $10^{-2}$ , which acetic acid can barely acquire even in concentrated solution. Also it is not surprising that the zirconium tetra-acetate prepared (Rosenheim and Hertzmann, *Ber.*, 1907, 40, 810) by dissolving anhydrous zirconium chloride in boiling anhydrous acetic acid hydrolyses completely and rapidly in water.

FIG. 1.

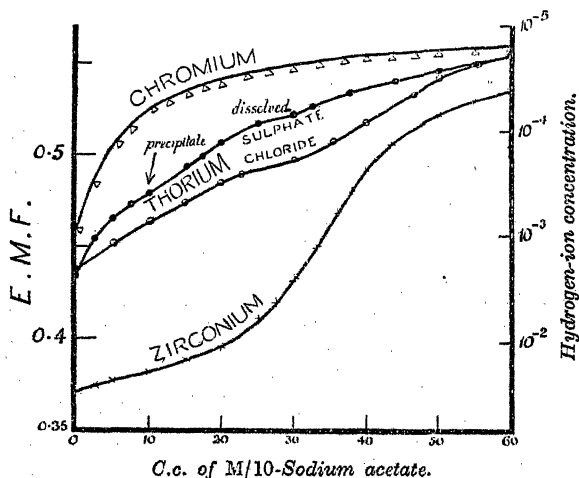


Fig. 1 shows the titration curve of 100 c.c. of  $M/100$ -zirconium chloride and  $N/10$ -sodium acetate at  $18^\circ$ . The solution remained clear throughout the titration. The extent to which the sodium acetate reacted with the zirconium chloride may be deduced from the hydrogen-ion concentrations of the solution when more than 40 c.c. (i.e., 4 mols. of  $\text{NaAc} : 1$  mol. of  $\text{ZrCl}_4$ ) of sodium acetate had been added. These are in Table I,  $E$  being the *E.M.F.* of the hydrogen electrode measured against a  $N$ -calomel electrode.

TABLE I.

C.c. of $N/10$ -NaAc.	$E$ .	$p_H$ .	$p_H$ calc.
40	0.392	3.62	3.15
60	0.536	4.38	4.34
80	0.553	4.69	4.64
100	0.560	4.80	4.81

The values given in the last column were calculated on the assumption that no acetic acid had combined with the zirconium hydroxide, the reaction supposed to have taken place being  $\text{ZrCl}_4 + 4\text{NaAc} + 4\text{H}_2\text{O} \rightarrow \text{Zr}(\text{OH})_4 + 4\text{HAc} + 4\text{NaCl}$ , and that the hydrogen-ion concentrations of the solution were due to the equilibria between these ions, the acetate ions from the sodium acetate (taken as 79% dissociated), and the acetic acid.

The agreement between the calculated and the observed values of  $p_{\text{H}}$  for additions of 60, 80, and 100 c.c. of sodium acetate seems to confirm the view that the solution, although quite clear, must have contained uncombined zirconium hydroxide. There is, however, no agreement between the values of  $p_{\text{H}}$  for the addition of 40 c.c. of sodium acetate; the higher, observed  $p_{\text{H}}$  is probably to be attributed to the presence of undecomposed sodium acetate, and not merely to the dissociation of all the acetic acid shown in the equation. It has been found from an acetic acid titration curve (see Prideaux, "Theory of Indicators," 1917, p. 226) that the observed value of  $p_{\text{H}}$  is 3.62 for an acetic acid solution which has been neutralised to the extent of 9% by sodium hydroxide. (In titrations of dilute solutions of weak acids the concentration of the solution has very little effect on the  $p_{\text{H}}$  ruling during the major part of the titration, the variations in  $p_{\text{H}}$  occurring at the beginning and the end.) In the zirconium titration, this proportion of acetic acid neutralised corresponds to 3.6 c.c. (*i.e.*, 9% of 40) of *N*/10-sodium acetate having remained unattacked, and therefore the reaction at this stage may be represented by the following scheme, 4 mols. of sodium acetate having been added to 1 mol. of zirconium chloride:  $4\text{NaAc} + \text{ZrCl}_4 + 3.64\text{H}_2\text{O} \rightarrow \text{ZrCl}_{0.36}(\text{OH})_{3.64} + 3.64\text{HAc} + 0.36\text{NaAc}$ . A highly basic zirconium chloride was therefore present in the solution. Its composition happens to be similar to that of the basic zirconium chloride,  $\text{ZrCl}_{0.5}(\text{OH})_{3.5}$ , present during the greater part of the alkali titration of zirconium chloride solution (J., 1925, 127, 2135).

The agreement of the observed with the calculated value of  $p_{\text{H}}$  obtained when an excess of sodium acetate had been added shows that the chloride which had earlier been attached to the zirconium hydroxide reacted with sodium acetate. It seems evident that the zirconium hydroxide was present in the solution in a colloidal state, although the solution was clear, probably owing to some slight solvent action of the acetic acid. Boiling brought about its slow decomposition.

The titrated solution was precipitable with alkalis, a precipitate first appearing when 1.2 equivalents of *N*/10-sodium hydroxide had been added.

*Thorium.*—Under certain conditions, sodium acetate produces a precipitate from thorium sulphate solutions, but not from those of thorium chloride. Two hydrogen electrode titrations were carried out, one of 100 c.c. of 0.01*M*-thorium chloride and the other of 100 c.c. of 0.01*M*-thorium sulphate, with *N*/10-sodium acetate. The curves are given in Fig. 1. Precipitation from the sulphate solution began when 10 c.c. of sodium acetate had been added and  $p_H$  3.4 attained (the precipitation value of  $p_H$  is 3.5 for thorium hydroxide) and appeared to be at a maximum when 25 c.c. had been added, but after the addition of 30 c.c. the precipitate, which was chiefly basic sulphate, dissolved and a clear solution was obtained. No trace of a precipitate formed in the thorium chloride solution under these conditions. The two titration curves converged at 60 c.c. and then became coincident, at least during the addition of the next 40 c.c. of sodium acetate.

The changes in hydrogen-ion concentration which occurred after 60 c.c. of sodium acetate had been added are indicated by the data : 80 c.c.,  $p_H$  4.97 ; 100 c.c.,  $p_H$  5.15, and were such as would be caused by the presence of acetic acid in amounts varying from 1.5 to 1.9 equivalents per one atom of thorium. It appears, therefore, that the thorium hydroxide present in these solutions was associated with at least 2 equivalents of acetate radical. The fact that the solutions were quite clear, although the precipitation value of  $p_H$ , 3.5, for the hydroxide had been exceeded, seems to indicate that the thorium-ion concentration had become considerably reduced by the change which had taken place in the solution, a change which might have been due to the formation of complex ions, or, perhaps more probably, to the formation of basic thorium acetate micelles which were capable of undergoing a different kind of ionisation.

The precipitate Haber obtained by boiling a thorium chloride solution with sodium acetate (*Monatsh.*, 1897, **18**, 687) is interesting, in that it contained 2 equivalents of acetate to one atom of thorium.

The precipitation of basic thorium sulphate from thorium sulphate solutions by sodium acetate seems to be accounted for by the tendency of sulphates of weak bases to form fairly stable basic sulphates in solution (compare zirconium sulphate, *J.*, 1925, **127**, 2140). The sodium acetate added to the 0.01*M*-thorium chloride solution had a continuous hydrolysing action, shown in the curve by the greater hydrogen-ion concentrations ruling during the early part of the reaction, whereas when it was added to the thorium sulphate solution hydrolysis was somewhat impeded, with the result that basic thorium sulphate was precipitated.

Acetic acid may have some solvent action on thorium hydroxide, for the hydrogen-ion concentrations of dilute solutions of the acid



are a little greater than that at which thorium hydroxide is normally precipitated ( $p_H$  3.5). This solvent action may be responsible for the holding of thorium hydroxide in solution at a  $p_H$  greater than 3.5, by causing, through the formation of comparatively inert basic thorium acetate micelles, the concentration of thorium ions to be so reduced that the solubility product of thorium hydroxide is not exceeded.

*Chromium.*—Substances containing chromium and the acetate radical have been the subject of many investigations, chiefly by Weinland and his collaborators (see Weinland, "Einführung in der Chemie der Komplex-Verbindungen," Stuttgart, 1919). Their chief interest lies in the remarkable colour changes which they exhibit on becoming more and more basic; *e.g.*, the green solution of chromium acetate itself, on addition of alkali, may remain green or become red or reddish-violet according to conditions such as time of keeping or of boiling (compare Recoura, *Compt. rend.*, 1899, **129**, 158, 208). Weinland and Büttner (*Z. anorg. Chem.*, 1912, **75**, 293) claim that these colours are due to salts of one or more complex "acetato-chromium" bases, whose constitutions are supposed to be accounted for by the co-ordination theory. The fact that these so-called bases, although essentially basic substances, contain varying amounts of acetate, *viz.*, 2.67, 2.33, 2.17, 2, or 1.5 equivalents of acetate for each atom of chromium, suggests that the colours may be due to the basic acetates themselves, and this view is supported by the experiments now to be described.

The curve in Fig. 1 represents the titration of 100 c.c. of 0.01*M*-chrome alum with *N*/10-sodium acetate. The  $p_H$ , which was 4.80 when 60 c.c. of sodium acetate had been added, became, on addition of 100 c.c., 5.02, and only just fell short of the precipitation value (5.34) for the hydroxide. The failure of the sodium acetate to produce a higher  $p_H$  after the theoretical quantity (60 c.c.) had been added was due to the "buffering" effect of the liberated acetic acid. It was pointed out in previous papers that in salts of chromium with strong acids one equivalent of the acid radical is loosely bound and reacts with alkali-metal salts of weak acids as if it were free acid, liberating an equivalent quantity of weak acid. In the present titration, this would correspond to the setting free of 20 c.c. of *N*/10-acetic acid. An idea of the amount of acetic acid actually liberated may be obtained from the fact that the  $p_H$  produced on addition of 60 c.c. of sodium acetate was the same as that produced by neutralising 60% of the acid in *N*/10- or *N*/100-acetic acid with sodium hydroxide. It seems certain, therefore, that the solution, besides containing an appreciable amount of free acetic acid, contained also basic chromium acetate aggregates capable of supplying

acetate ions to the solution. The solution remained green throughout the titration and was precipitated by alkalis, but the precipitate redissolved on addition of less alkali than would have been necessary had the precipitate been obtained from a solution of a chromium salt of a strong acid.

Chromium combined with acetic acid sometimes resists precipitation by alkalis. This property depends on the treatment to which the solution has been subjected, as may be seen from the data in Table II: under *a* is the number of c.c. of *N*/10-sodium acetate that were added to 10 c.c. of *M*/10-chrome alum, and in the last two columns are the equivs. of *N*/10-sodium hydroxide (per 1 atom of chromium) that were required to produce (*b*) a precipitate and (*c*) neutrality to phenolphthalein.

TABLE II.

<i>a.</i>	Remarks.	Colour.	<i>b.</i>	<i>c.</i>
60	Violet chrome alum solution used, and mixed at room temperature.	Green.	0.64	2.81
"	Green chrome alum solution, mixed at room temperature.	"	1.18	2.67
"	Reactants mixed, boiled, and cooled to room temperature.	Purplish-green.	No ppte.	1.89
"	Alkali added to boiling reactants.	Green.	2.21	2.21 to 2.80
"	Reaction mixture on protracted boiling became completely precipitated as basic acetate.	Solution colourless.	—	2.51
"	Violet chrome alum; mixture kept for 24 hours.	Bluish-red.	1.76	2.38
120	"	Purple.	No ppte.; solution green.	2.11
"	Mixture boiled for 20 minutes and kept for 24 hours.	Green.	No ppte.	2.22

It will be noticed that in one case prolonged boiling caused basic chromium acetate to be precipitated completely; 2.51 equivs. of acetic acid remained in the solution, and therefore the composition of the precipitate was  $\text{CrAc}_{0.49}(\text{OH})_{2.51} \cdot x\text{H}_2\text{O}$ . In three instances, solutions were obtained which were non-precipitable with sodium hydroxide; one of these, which contained a larger proportion of sodium acetate, was purple and had been rendered non-precipitable merely by keeping, the other two had been rendered so by initial boiling. The amounts of alkali required to make the three solutions alkaline to phenolphthalein, being approximately 2 equivalents to one atom of chromium, suggest that about 1 equivalent of acetate radical was linked to the chromium hydroxide in an inert manner,

probably in a colloidal complex. The reaction which took place while the chromium solution was thus changed by boiling may perhaps be represented by the following equation:  $\text{Cr}_2(\text{SO}_4)_3 + 6\text{NaAc} + 2x\text{H}_2\text{O} = 2\text{CrAc}_{3-x}(\text{OH})_x + 2x\text{HAc} + 3\text{Na}_2\text{SO}_4$ . The data in the table show that the value of  $x$  in the basic complex, after any acid this may have set free by hydrolysis had been neutralised, varied from 1.89 to 2.22.

A further electrometric titration was carried out to ascertain whether the acid liberated in the formation of the basic complex was a complex acid or merely acetic acid. A mixture of 120 c.c. of  $N/10$ -sodium acetate with 10 c.c. of  $M/10$ -chrome alum was rendered non-precipitable by boiling for 5 minutes, and the reddish-violet solution cooled to  $18^\circ$ . The *E.M.F.* of the hydrogen electrode, compared with the *N*-calomel electrode, was 0.551 volt, and therefore  $p_{\text{H}}$  was 4.64. The first section of the curve representing the titration with  $N/10$ -sodium hydroxide was similar to that of acetic acid, and the free acid became neutralised when 46.8 c.c. of alkali had been added. The solution remained violet throughout the titration, but the violet solution to which 60 c.c. of  $N/10$ -sodium hydroxide had been added appeared colloidal after 24 hours, and was precipitated on continued boiling. If the basic acetate complex did not undergo any hydrolysis during the titration, the free acid was equivalent to 46.8 c.c. of  $N/10$ -acid and the excess of sodium acetate to 60 c.c. of  $N/10$ , 13.2 c.c. of  $N/10$ -sodium acetate having been decomposed. The sodium acetate being assumed to be 79% ionised, and the free acid to be acetic ( $K = 1.8 \times 10^{-5}$ ), the hydrogen-ion concentration of the solution should have been  $10^{-4.74}$ , which is in fair agreement with the observed value. The experiment seems, therefore, to confirm the view expressed by the equation.

When the solution is rendered inert to alkalis merely by keeping, the hydrolysis is not so marked, and probably much of the acetic acid is in a state of loose combination. The change that renders the basic chromium acetate complex inert is probably similar to that which chromium hydroxide undergoes slowly on keeping, and rapidly on boiling, in contact with its mother-liquor. The hydroxide becomes considerably less reactive and requires an appreciable time for dissolution in acids. If the basic chromium acetate complexes are colloidal, they may undergo some ageing or stabilising process and their size may have some effect on the absorptive power for light which modifies the colour of the solution.

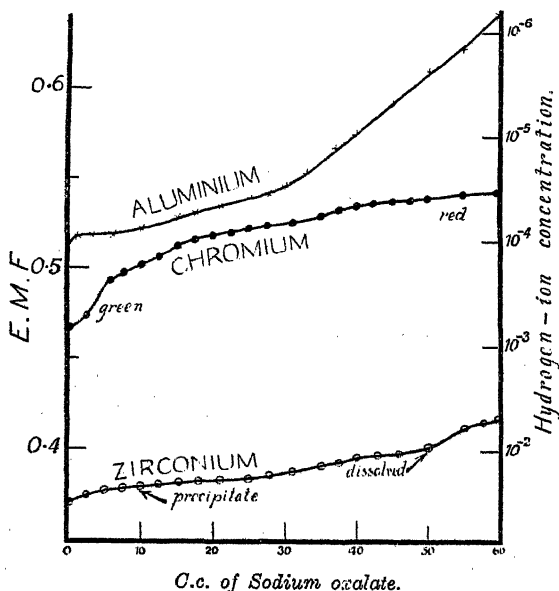
## II. Sodium Oxalate Titrations.

Oxalic acid is a strong acid in regard to its first stage of ionisation, but fairly weak in respect to its second stage,  $K_2$  being  $1.3 \times 10^{-4}$

(J., 1925, 127, 1905). The titrations described in this section were therefore carried out to see if the latter had any influence on the reactions between sodium oxalate and salts of weak bases. It is significant that the hydroxides which are generally supposed to enter into complex formation with oxalates are weak bases, all of which are precipitated by alkalis from solutions whose hydron concentrations are greater than  $10^{-7}$  (compare Schäfer and Abegg, *Z. anorg. Chem.*, 1906, 14, 293).

*Zirconium.*—As zirconium hydroxide is ordinarily precipitated from solutions whose hydrogen-ion concentrations are greater than

FIG. 2.



$10^{-2}$ , it was considered that the hydrogen-ions arising from the second dissociation of oxalic acid would be too few to affect the dissolution of the hydroxide.

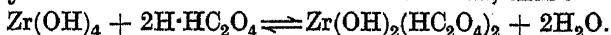
The reaction between 100 c.c. of  $M/100$ -zirconium chloride and  $N/10$ -sodium oxalate was studied by means of the hydrogen electrode. The variation in hydrogen-ion concentration is given in Fig. 2. A gelatinous precipitate appeared when 10 c.c. of sodium oxalate had been added, and precipitation was at a maximum with 40 c.c., after which the precipitate began to dissolve; the solution became quite clear again on addition of 50 c.c. The precipitate obtained when 20 c.c. of sodium oxalate had been added had the composition  $\text{Zr}(\text{OH})_{2.69}(\text{C}_2\text{O}_4)_{0.69} \cdot x\text{H}_2\text{O}$ . The precipitates obtained by Venable

and Baskerville (*J. Amer. Chem. Soc.*, 1897, **19**, 11) on treating zirconium chloride solutions with a saturated solution of oxalic acid had the compositions  $\text{Zr}(\text{OH})_{2.67}(\text{C}_2\text{O}_4)_{0.67}$  and  $\text{Zr}(\text{OH})_{2.4}(\text{C}_2\text{O}_4)_{0.8}$ .

The complex formed on re-solution of the basic zirconium oxalate was not readily precipitated with alkalis: *e.g.*, the acid liberated by the interaction of 100 c.c. of *M*/100-zirconium tetrachloride and 100 c.c. of *N*/10-sodium oxalate was neutralised (phenolphthalein) by 35.3 c.c. of *N*/10-sodium hydroxide without a precipitate forming, and indeed only a slight opalescence was produced when sufficient alkali had been added to convert all the zirconium salt into the hydroxide and the solution boiled (40 c.c.).

The titration curve shows that a large concentration of hydrogen ions persisted throughout the whole reaction,  $p_{\text{H}}$  being 2.32 at 60 c.c., 3.10 at 80 c.c., and 3.64 at 100 c.c. There occurred a small inflexion just after 50 c.c. of sodium oxalate had been added, which indicated the stage at which oxalate ions had been added in an amount just sufficient to combine with the hydrogen ions from the first stage of dissociation to form  $\text{HC}_2\text{O}_4'$  ions (compare oxalic acid titration curve, *loc. cit.*). Thereafter the hydrogen-ion concentration arose from the ionic equilibrium  $\text{HC}_2\text{O}_4' \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4''$ .

The zirconium hydroxide is present in the oxalate solution probably in the colloidal state, having been rendered so by combination with or adsorption of oxalate ions through the interplay of slight chemical forces. As the first stage of the ionisation of oxalic acid is that of a strong acid, there is reason to believe that this acid would, like hydrochloric or nitric acid, be capable of maintaining zirconium hydroxide in solution. Two molecules of oxalic acid, which on valency grounds should react with zirconium hydroxide to form the unknown zirconium oxalate,  $\text{Zr}(\text{C}_2\text{O}_4)_2$ , are only capable of reacting as if they were two molecules of a monobasic acid, thus:



The basic zirconium hydro-oxalate, by analogy with the chloride (*q.v.*), would be strongly hydrolysed in solution, giving highly basic hydro-oxalate aggregates which would tend to remain in colloidal solution by virtue of the tendency which they may have to react with the hydrogen ions from the  $\text{HC}_2\text{O}_4'$  ions. The fact that sodium hydroxide does not readily precipitate zirconium hydroxide from oxalate solutions seems to show that zirconium ions are absent, or nearly so, from the solutions.

Sodium oxalate when added to a zirconium sulphate solution did not give a precipitate. An attempt was made to follow the changes in hydron concentration during the addition of sodium oxalate by means of the hydrogen electrode, but the entry of a little potassium chloride, used in the junction liquid, into the zirconium sulphate

solution immediately rendered it precipitable. *M*/100-Zirconium sulphate (100 c.c.) was titrated and precipitation due to the potassium chloride began, but the precipitate did not redissolve until 85 c.c. of the oxalate solution had been added.

The clear solution obtained by adding sodium oxalate in not too great an excess to a zirconium sulphate solution gave a precipitate on addition of a little electrolyte, *e.g.*, the chloride or nitrate of sodium or potassium.

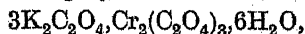
*Chromium.*—The curve in Fig. 2 is that of the titration of 100 c.c. of *M*/100-chrome alum with *M*/10-sodium oxalate. The solution was green initially, but became red towards the end of the titration. The diagram shows a very slight inflexion just after 30 c.c. of sodium oxalate had been added, *i.e.*, 3 mols.  $\text{Na}_2\text{C}_2\text{O}_4$  to 1 mol.  $\text{Cr}_2(\text{SO}_4)_3$ , but the curve does not thereafter assume the upward course which it would take had simple double decomposition taken place. The very gradual diminution in hydron concentration caused by the addition of sodium oxalate was due to the "buffering" action of the hydro-oxalate ions which had failed to react. The hydrogen-ion concentration at the end of the titration was  $10^{-4.4}$ , which was greater than the precipitation value,  $10^{-5.3}$ , for the hydroxide, but gradually approached it when larger quantities of sodium oxalate were employed. The solution to which 60 c.c. of *M*/10-sodium oxalate had been added was afterwards titrated with *N*/10-sodium hydroxide by means of the hydrogen electrode. Precipitation began when 1.85 equivalents had been added ( $p_{\text{H}}$  5.4); thereafter the alkali caused only a partial precipitation and the graph of the change in  $p_{\text{H}}$  plotted against the amount of alkali added was rectilinear instead of curved, as is usually the case for precipitation by alkali. The slow change in hydron concentration appears to have been caused by slight decomposition of the basic complex.

Some experiments were made to ascertain the conditions which rendered the solutions non-precipitable by alkalis. A mixture of *M*/10-chrome alum (1 mol.) and *M*/10-sodium oxalate (3 or 6 mols.) at room temperature gave a precipitate on treatment with *N*/10-sodium hydroxide; but if it had been first boiled and then cooled, no precipitate was obtained. Non-precipitable solutions were also produced by keeping. For example, two solutions, each 250 c.c., containing 30 and 60 c.c., respectively, of *M*/10-sodium oxalate and 10 c.c. of *M*/10-chrome alum, were kept over-night; the one containing the larger quantity of oxalate failed to give a precipitate with alkali.

An interesting gradation in colour was observed in a series of solutions, of the same concentration with respect to chrome alum but containing different quantities of sodium oxalate, the smallest

being 3 mols. (to 1 mol. of the sulphate), which had been boiled for the same length of time (a few minutes) and then kept over-night. They were all red in transmitted light, but had a green tinge in reflected light; the redness increased in intensity with increasing molar proportion of sodium oxalate. This may have been due to the effect of the diminishing hydrogen-ion concentration on the basic chromium oxalate complexes, produced by the increasing amounts of sodium oxalate. The solutions gave no precipitate in the cold on treatment with alkali, but a precipitate slowly formed on boiling. If the alkali was added in amounts just sufficient to convert the chromium salt into chromium hydroxide, precipitation took place after about a day. These alkaline solutions were also coagulated by the addition of 2 or 3 c.c. of saturated potassium chloride solution. Solutions which had been rendered non-precipitable by keeping only were very slightly more hydrolysed than the others.

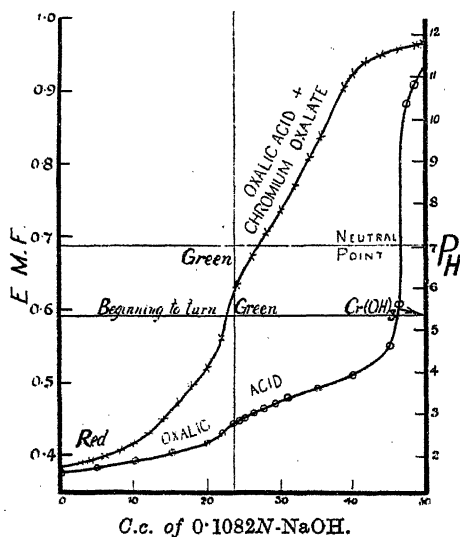
An oxalic acid solution of chromium hydroxide was prepared by boiling a chromic acid solution with oxalic acid until reduction was complete. The solution so obtained was claret-red and was not immediately precipitable by alkalis; on evaporation, it gave a green mass and oxalic acid crystals. From such a solution another was prepared which contained oxalic acid and chromium hydroxide in the proportions required by Werner's hypothetical tribasic chromi-oxalic acid,  $H_3[Cr(C_2O_4)_3]$  (*Ber.*, 1912, 45, 3061). The molar ratio may therefore be represented as  $3H_2C_2O_4 : Cr_2(C_2O_4)_3$ . The quantity of free and combined oxalic acid in 100 c.c. of the solution was equivalent to 51 c.c. of *N*/10-alkali, and on the latter method of representing the formula one-half of this, 25.5 c.c., may be regarded as combined with the chromium. This solution was titrated with 0.1082*N*-sodium hydroxide at 18° by means of the hydrogen electrode. The titration curve is given in Fig. 3. (The lower curve represents the titration, with the same alkali, of 51 c.c. of *N*/10-oxalic acid diluted to 100 c.c.) In reply to the objection that such a solution cannot possibly supply any information concerning Werner's hypothetical acid, it may be mentioned that the acid solution has the peculiar properties of Gregory's double salt,



which Werner regarded as a salt,  $K_3[Cr(C_2O_4)_3]$ , of his complex hypothetical acid and named potassium trioxalochromiate. The titration curve gives no evidence of the existence of a tribasic acid, but is composed of two distinct sections. Although no precipitate formed, it is significant that the claret-red solution began to turn green just when the hydron concentration had become that at which chromium hydroxide is normally precipitated. This suggests that the colour is in some way related to the hydroxide itself.

The fact that the first half of the reaction terminated with an inflexion in the curve and a change in colour seems to be connected with the great difference between the two stages of ionisation of oxalic acid. The simplest explanation is to regard the chromium in the original solution as combined almost entirely with  $\text{HC}_2\text{O}_4$  radicals, thus:  $\text{Cr}(\text{OH})_2 + 3\text{H}\cdot\text{HC}_2\text{O}_4 \rightarrow \text{Cr}(\text{HC}_2\text{O}_4)_3 + 3\text{H}_2\text{O}$ . The relatively large hydrion concentration could then be accounted for by slight hydrolysis having taken place owing to some little reaction with the hydrions from the hydro-oxalate ions. The first half of the titration would therefore be mainly that of the hydrogen ions from the large amount of  $\text{HC}_2\text{O}_4$  ions with the added hydroxyl ions, and

FIG. 3.



therefore the range of hydrion concentration covered would be approximately that covered in the second half of the oxalic acid titration. The high initial concentrations in the chromium titration being excluded, it will be seen that the two ranges are comparable. When exactly half the theoretical amount of sodium hydroxide had been added, the reaction  $3\text{NaOH} + \text{Cr}(\text{HC}_2\text{O}_4)_3 \rightleftharpoons 3\text{H}_2\text{O} + \text{Cr}(\text{NaC}_2\text{O}_4)_3$  may be considered to have taken place, and the second half of the sodium hydroxide would therefore have to react with the double sodium chromium oxalate to form a basic oxalate, probably associated with some sodium. The second portion of the chromium curve shows that only a part of the theoretical amount of the alkali had reacted, for the solution became alkaline on addition of considerably less sodium hydroxide than in the case of the oxalic acid



titration. Therefore, if  $x$  be the fraction of sodium hydroxide which had reacted, the reaction may be represented by the equation:  $\text{Cr}(\text{NaC}_2\text{O}_4)_3 + 3x\text{NaOH} \rightleftharpoons \text{Cr}(\text{OH})_{3x}(\text{NaC}_2\text{O}_4)_{3-3x} + 3x\text{Na}_2\text{C}_2\text{O}_4$ .

The basic chromium oxalate complex is probably capable of ionising, but not so much so that it would produce in the solution the concentration of chromium ions requisite for precipitation. From the titrated solution to which 60 c.c. of 0.1082*N*-sodium hydroxide had been added, *i.e.*, 12.9 c.c. in excess of that required for the complete decomposition of the chromium oxalate, the chromium was completely precipitated after 24 hours, and, like the previous solutions, those which had been rendered just alkaline were also immediately coagulable on addition of a few c.c. of saturated potassium chloride solution and shaking. These observations seem to point to the colloidal nature of the basic oxalate complexes.

The absorption spectra of solutions representing different stages of the titration were examined. The solutions corresponding to the first half of the reaction absorbed light in the red, yellowish-green, and extreme blue regions. The absorption in the blue region was fairly uniform throughout the titration, whereas the absorption band in the green became considerably reduced in the second half. The chief change in absorption appeared suddenly in the red region almost immediately after the middle point of the titration had been passed; for the solution corresponding to the end of the titration, the band extended over the whole red field and partly into the orange. These absorptions were probably due to the size of the semi-colloidal particles. Lapraik's researches on the absorption spectra of chromium solutions (*J. pr. Chem.*, 1892, 47, 305) included that of a colloidal solution of chromium hydroxide prepared by dialysing chromium chloride for some months, and also of chromium hydroxide suspended in water. He stated that the close resemblance between the absorption spectra of solutions of chromium hydroxide in several organic acids, including oxalic and some hydroxy-acids, despite the great difference in the molecular complexity of the acids used as solvents, suggested the probability of the absorption spectra being due mainly to the chromium hydroxide or oxide, and not to its compounds with the solvents. This constitutes strong support for the view that solutions of chromium salts of weak acids are essentially colloidal.

E. A. Werner (*J.*, 1904, 85, 1438) made the interesting observation that chromium hydroxide dissolves in hot oxalic acid solution to the extent required by the formula  $\text{Cr}_2(\text{C}_2\text{O}_4)_3$ . This, however, is no evidence for the existence of chromium oxalate in the solution, for solutions of the chromium salts of strong acids may be rendered basic beyond the point corresponding with the formula  $\text{Cr}(\text{OH})\text{R}_2$ ,

before any precipitation takes place. Hence in Werner's solution probably little more than the ions from the first stage of the dissociation of the oxalic acid combined with the chromium hydroxide, and this was present largely as a basic chromium hydro-oxalate; a small proportion of the second-stage hydrogen ions may have entered into reaction. Such an explanation would account for the anomalous conductivity data obtained by Rosenheim (*Z. anorg. Chem.*, 1896, **11**, 225) for a solution containing chromium oxide and oxalic acid in the proportion 1 : 3; he could obtain from the data no conclusive evidence that the substance in solution was either a free complex acid or a chromium salt of a complex chromioxalic acid.

The formula of the hypothetical tribasic chromioxalic acid is based on Rosenheim's measurements (*Z. anorg. Chem.*, 1896, **11**, 196, 225; 1899, **21**, 8) of the conductivity of solutions of double oxalates having the formula  $3R_2C_2O_4 \cdot Cr_2(C_2O_4)_3 \cdot xH_2O$ , where R is K, Na, or  $NH_4$ . Regarding these as complex salts,  $R_3[Cr(C_2O_4)_3]$ , he found that the difference between  $\Lambda_{1024}$  and  $\Lambda_{32}$  (where  $\Lambda$  is the conductivity of  $1/3R_3[Cr(C_2O_4)_3]$ )

varied from 32.4 to 35.8 for the three salts, and thence deduced the tribasicity of the complex acid,  $H_3[Cr(C_2O_4)_3]$ . It may be pointed out that there is no accord between Rosenheim's data for the potassium salt solutions and the earlier values of Kistiakovsky (*Z. physikal. Chem.*, 1890, **6**, 98). Rosenheim's figures also show that the ammonium salt is much more ionised than the potassium salt. The conductivities of the sodium and ammonium salts measured by Burrows and Walker (J., 1923, **123**, 2738) are somewhat lower than those of Rosenheim, but the differences  $\Lambda_{1024} - \Lambda_{32}$  are 29.3 and 32.9, respectively. By means of their cryoscopic and conductivity measurements these authors were able to show that in those solutions which were more dilute than 1/16-molar the number of ions into which each molecule of the salt dissociated was greater than 4. They concluded that it is only in comparatively concentrated solutions, greater than  $M/10$ , that the salt  $R_3[Cr_2(C_2O_4)_3]$  dissociates into  $3R^+$  and  $[Cr(C_2O_4)_3]^{3-}$ , and that at higher dilutions either the salt hydrolyses, giving ROH and  $H_3[Cr(C_2O_4)_3]$ , or the complex anion dissociates still further. The evidence for the existence of the complex tribasic chromioxalic acid is therefore inconclusive.

Some experiments have been carried out on Gregory's salt,  $3K_2C_2O_4 \cdot Cr_2(C_2O_4)_3 \cdot 6H_2O$  (*vide* Graham, "Chemical and Physical Researches," Edinburgh, 1876, p. 369). It was obtained in deep blue needles by allowing to crystallise a solution, containing chromic anhydride, potassium oxalate, and an excess of oxalic acid, which had been boiled until the anhydride was completely reduced

[Found : Cr, 10.7 ;  $C_2O_4$ , estimated by Burrows and Walker's method (*loc. cit.*), 54.1. Calc. : Cr, 10.7 ;  $C_2O_4$ , 54.2%].

On addition of  $N/10$ -sodium hydroxide to an  $M/120$ -solution of the salt there was no immediate reaction, as shown by hydrogen electrode measurements, but the red solution on becoming alkaline turned green, and when sufficient alkali had been added to convert the chromium oxalate into chromium hydroxide and the solution kept for 12 hours, it became opalescent and addition of a little potassium chloride caused precipitation. Addition of potassium chloride to a solution rendered just alkaline produced opalescence within a few minutes and the chromium was completely precipitated as the hydroxide in the course of 2 hours.

Werner made use of Gregory's salt in the development of his theory of "mirror-image isomerism." He suggested that the substance, regarded as the salt of a complex acid, should show a type of molecular asymmetry and be resolvable into optically active isomerides. The six molecules of water were regarded as water of crystallisation, and not of constitution as in the case of the hexahydrated chromium chloride. He achieved a fugitive resolution, by means of strychnine, in which water must have played an important part, for the optical activity disappeared much more quickly in aqueous than in acetone solutions. Jaeger (*Rec. trav. chim.*, 1919, **38**, 245) obtained much larger rotations. Rideal and Thomas (*J.*, 1922, **121**, 196) found that the resolved salt on dissolution left a small, insoluble residue. This is surprising in view of the great ease with which the double oxalate dissolves. Their suggestion that the speedy loss in optical activity is due to decomposition of the complex anion into a less complex one seems to be confirmed by the *E.M.F.* measurements of Thomas and Fraser (*J.*, 1923, **123**, 2973).

As water appeared to be the important factor in those optical rotation experiments, measurements have been made with the hydrogen electrode to ascertain if any parallel hydrolytic change occurs. The *P.D.* between a hydrogen electrode immersed in 100 c.c. of water at 18° and the normal calomel electrode, with saturated potassium chloride solution as junction liquid, was measured ; 0.8123 g. of Gregory's salt was then rapidly dissolved in the water, and the *E.M.F.* observed every few minutes over a period of several hours. The results, which are in Table III, showed that

TABLE III.

Mins. ....	0	5	15	29	41	52
$p_H$ .....	6.67	7.03	7.05	6.22	5.69	5.64
	(water)					
Mins. ....	70	93	105	138	180	20 hrs.
$p_H$ .....	5.56	5.49	5.39	5.36	5.32	5.33

immediately following dissolution the hydron concentration gradually increased until the  $p_H$  had become 5.49 (93 minutes); thereafter the change was much slower and the  $p_H$  became constant (5.33) after 12 hours and remained so during the next 20 hours. This  $p_H$  happens to be that at which chromium hydroxide is ordinarily precipitated. If the chromium oxalate in the salt were in a condition similar to that of the chromium salts of strong acids, a considerably higher hydrogen-ion concentration would have been produced. On referring to Fig. 3, it will be seen that the  $p_H$  (6.0) attained when the quantity of sodium hydroxide added was that required to form  $3Na_2C_2O_4 \cdot Cr_2(C_2O_4)_3$  (indicated by the vertical line through the mid-point) was a little higher than the precipitation  $p_H$  of chromium hydroxide, probably owing to some decomposition of the oxalate complex having taken place. It therefore seems likely that the existence of the double salt may be due to the two different degrees of reactivity of oxalic acid, and that the change in hydron concentration that occurs on its passing into solution may be due to the formation of basic complexes as suggested by the solution reaching the precipitation  $p_H$  of the hydroxide.

The concentration of oxalate ions in these complex salt solutions is small, for calcium chloride fails to give an immediate precipitate. Instead of being due to a complex anion, this may be equally well accounted for by the view now put forward, that the greater part of the oxalate ions is, in effect, removed from the solution in the form of colloidal complexes.

The fact that double oxalates of the general formula



exist, where M may be trivalent iron, chromium, or aluminium, seems to be attributable to the nature of oxalic acid. The bases of these elements are so weak that it is exceedingly doubtful whether they are capable of entering into reaction to form normal oxalates, and yet in conjunction with the alkali metals they form well-defined compounds. There seems to be little doubt that the weak bases enter into combination with the  $HC_2O_4$ -ions, leaving the  $C_2O_4$  ions to the alkali metals.

*Aluminium.*—The curve in Fig. 2 represents the hydrogen electrode titration of 100 c.c. of 0.005*M*-aluminium sulphate with 0.05*M*-sodium oxalate. No precipitate appeared, although the precipitation  $p_H$  of aluminium hydroxide was soon exceeded. The curve was only slightly inclined during the addition of the first 30 c.c. of sodium oxalate [i.e., 3 mols.  $Na_2C_2O_4$  to 1 mol.  $Al_2(SO_4)_3$ ] and the corresponding  $p_H$ 's differed but slightly from the precipitation  $p_H$  (4.14) of aluminium hydroxide, which was attained when 10 c.c. of sodium oxalate had been added. This suggests that aluminium

hydroxide, although it was not precipitated, existed in the solution in a more or less nascent state. Also the fact that the sodium oxalate in excess of 30 c.c. produced a gradual change in hydron concentration, instead of an almost instantaneous fall to a concentration of the order produced by free sodium oxalate, shows that equilibria were being set up between the hydro-oxalate ions, which had failed to react with the aluminium hydroxide, and the oxalate ions from the added sodium oxalate. After the addition of 100 c.c. of *N*/10-sodium oxalate, the solution was titrated with *N*/10-sodium hydroxide; it became alkaline to phenolphthalein when 2.13 equivalents of sodium hydroxide (to one atom of aluminium) had been added, but no precipitate formed. Three equivalents of alkali, which were sufficient to convert all the aluminium salt into hydroxide, were then added; a precipitate appeared only after some time.

### III. Sodium Tartrate Titrations.

Tartaric acid is comparatively weak in its first stage of ionisation,  $K_1 = 1.27 \times 10^{-3}$ , and much weaker in its second stage,  $K_2 = 9.65 \times 10^{-5}$  at 18° (J., 1925, 127, 1905). Of the metallic bases studied in these investigations, the only two that give basic tartrates on treatment with sodium tartrate are the very weak bases thorium and zirconia; these also dissolve in excess of the precipitant to give complex solutions which are not precipitable by alkalis. The reactions between zirconium, thorium, aluminium, beryllium, chromium, zinc, and lanthanum salts and *N*/10-sodium tartrate have been followed with the hydrogen and the normal calomel electrode. The titration curves of 100 c.c. of each of the solutions at 18° are in Fig. 4.

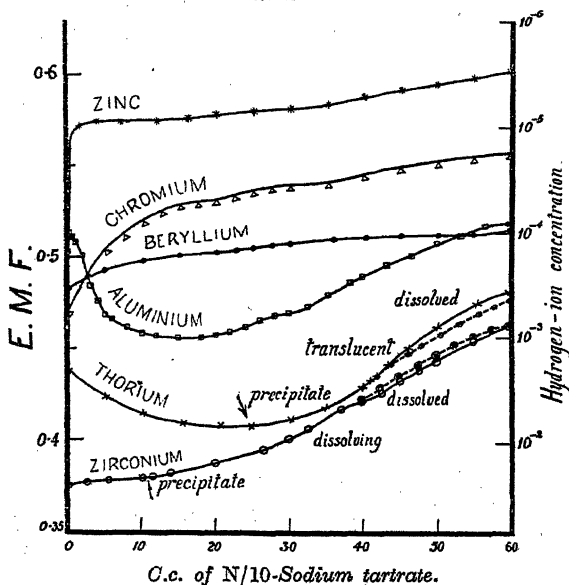
*Zirconium*.—The curve (Fig. 4) shows the changes in hydron concentration that occurred during the addition of *N*/10-sodium tartrate to 100 c.c. of *M*/100-zirconium chloride. A gelatinous basic tartrate began to be precipitated when 10 c.c. of sodium tartrate had been added ( $p_H$  1.66), but it began to redissolve on addition of 30 c.c. With 40 c.c., the solution was translucent, but became clear with 42.5 c.c.

The precipitate corresponding with the addition of 20 c.c. of *N*/10-sodium tartrate was produced by mixing large volumes of the reactants, the supernatant liquor being poured off, and the precipitate washed by decantation. It passed entirely into a translucent colloidal solution. The precipitate had therefore to be freed from the adhering liquor as completely as possible by pressing between filter-paper; some sodium tartrate, however, remained [Found in the air-dried precipitate:  $ZrO_2$ , 39.7; C (by "wet" combustion with chromic acid), 7.1%]. If the water content is neglected,

the composition of the precipitate may be expressed by the formula  $\text{ZrT}_{0.45}(\text{OH})_{3.1}$ .\*

In order to get some idea of the amount of titratable acid in these zirconium tartrate solutions, various quantities of  $N/10$ -sodium tartrate were added to 100 c.c. of  $M/100$ -zirconium chloride, and the resulting solutions titrated with  $N/10$ -sodium hydroxide. The results are in Table IV:  $a$  = c.c. of tartrate added, and  $b$  and  $c$

FIG. 4.



= c.c. of  $N/10$ -alkali required to produce neutrality to phenolphthalein at  $18^\circ$  and  $100^\circ$ , respectively.

TABLE IV.

$a$ .....	10	20	30	40	60	80
$b$ .....	33.2	33.1	33.0	33.1	33.2	33.2
$c$ .....	34.9	34.6	35.0	34.3	34.1	34.2

The alkali produced a precipitate, which did not redissolve, from the solution to which 10 c.c. of sodium tartrate had been added, but the precipitates that formed initially in the 20 c.c.- and 30 c.c.- solutions redissolved when 25 c.c. and 14 c.c., respectively, of the alkali had been added. If no hydrolysis of the complex tartrate occurred, the table shows that, no matter how much sodium tartrate

\* Throughout this paper T denotes  $\text{C}_4\text{H}_4\text{O}_6$ .

had been added, the quantity of free acid in the solution at 18° was equivalent to about 33.1 c.c. of *N*/10-sodium hydroxide, or 3.31 eqivs. to 1 atom of zirconium. Under these conditions, the simplest formula for the basic complex in these solutions is  $\text{ZrT}_{0.35}(\text{OH})_{3.3}$ , which is in fair agreement with that obtained for the imperfectly washed, basic precipitate, viz.,  $\text{ZrT}_{0.45}(\text{OH})_{3.1}$ .

To confirm the existence of this complex in solution, and to show that the free acid was tartaric, the following titration was made. The change in hydron concentration which occurred after 40 c.c. of *N*/10-sodium tartrate had been added was what would be expected to occur on addition of sodium tartrate to a solution containing free tartaric acid only. A solution (140 c.c.) was therefore prepared containing 33.1 c.c. of *N*/10-tartaric acid, which appears to be the amount of acid liberated on addition of the first 40 c.c. of sodium tartrate in the zirconium titration. The *E.M.F.* of the solution, measured with the hydrogen electrode against the normal calomel electrode, was 0.422 volt (the *E.M.F.* for the corresponding stage of the zirconium titration was 0.421 volt). Increasing quantities of *N*/10-sodium tartrate were now added; the voltages obtained are shown in the diagram by the broken line just above the zirconium curve. During the addition of the first 20 c.c. of *N*/10-sodium tartrate, i.e., corresponding to 60 c.c. in the zirconium titration, the broken curve lay at a distance representing 3 millivolts at most from the zirconium curve, but during the addition of the next 40 c.c. (i.e., corresponding with 60 to 100 c.c. in the zirconium titration) the two curves became coincident.

Tartaric acid also precipitates a basic tartrate from zirconium chloride solutions, but a considerably larger excess is required to effect its re-solution than in the case of sodium tartrate. For example, the precipitate formed when *N*/10-sodium tartrate was added to 100 c.c. of *M*/100-zirconium chloride solution required just over 40 c.c. for both precipitation and dissolution, whereas, when *N*/10-tartaric acid was used, re-solution did not occur until about 150 c.c. had been added. The precipitate so formed dissolved readily in alkali, and the composition of the soluble complex thereby produced appeared to be the same as that in the sodium tartrate solutions. It may be that re-solution was actually due to the sodium tartrate which was formed, as may be seen from the following experiment. The heavy, gelatinous precipitate produced by adding *N*/10-sodium hydroxide to a mixture of 100 c.c. of *M*/100-zirconium chloride and 40 c.c. of *N*/10-tartaric acid dissolved when about 45 c.c. had been added, and the solution became alkaline to phenolphthalein with 73.2 c.c., which shows that the composition of the complex must have been  $\text{ZrT}_{0.34}(\text{OH})_{3.32}$ .

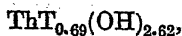
The last column of Table IV shows that the complexes underwent very little decomposition in boiling alkaline solution.

The solubility of the basic zirconium tartrate precipitates in sodium hydrogen tartrate is less than that in the neutral tartrate, but greater than that in the free acid. The limiting amount of sodium tartrate to be added to a zirconium chloride solution to render it non-precipitable by alkali appears to be about 1 molecular proportion. With this proportion, a precipitate is obtained, but it dissolves on the addition of alkali; at a stage, however, before the solution becomes alkaline.

*Thorium.*—The curve (Fig. 4) represents the titration of 100 c.c. of  $M/100$ -thorium chloride with  $N/10$ -sodium tartrate. It is remarkable in that it shows that the addition of a normal tartrate rendered the solution more acid and then produced a precipitate. The  $p_H$  of the original solution was 2.68, but had fallen to 2.15 on addition of 25 c.c. of sodium tartrate, when precipitation began. By analogy with the formation of other basic precipitates—chromates, borates, and carbonates (Britton, this vol., p. 125)—it would have been expected that the precipitation of a basic tartrate would not have taken place until the precipitation  $p_H$  of the hydroxide had been attained, *viz.*, 3.5. A basic tartrate of thorium may also be precipitated by free tartaric acid; precipitation began at  $p_H$  1.75 when 27.5 c.c. of 0.112*N*-tartaric acid were added to 100 c.c. of  $M/100$ -thorium tartrate, the large hydrion concentration being no doubt due to hydrochloric acid produced by hydrolysis.

The precipitates were flocculent and were not of definite composition. Haber's analyses (*Monatsh.*, 1897, **18**, 687) of precipitates obtained with tartaric acid, the water contents being disregarded, lay between those required for  $\text{ThT}(\text{OH})_2$  and  $\text{ThT}_{1.33}(\text{OH})_{1.33}$ . The basic tartrate produced above from sodium tartrate and thorium chloride contained still less tartrate. The precipitate obtained on addition of 30 c.c. of sodium tartrate was, when air-dried, amorphous and contained 45.51%  $\text{ThO}_2$  and 5.69% C (found by "wet" combustion), corresponding to the formula  $\text{ThO}_2 \cdot 0.69\text{T} \cdot 11.91\text{H}_2\text{O}$ , or, the water content being disregarded,  $\text{ThT}_{0.69}(\text{OH})_{2.62}$ .

Like basic zirconium tartrate, basic thorium tartrate redissolved when a little more than 40 c.c. of  $N/10$ -sodium tartrate had been added, *i.e.*, when the proportion was  $2\text{Na}_2\text{T} : \text{ThCl}_4$ . The acid liberated in the solution was equivalent to 26.2 c.c. of  $N/10$ -sodium hydroxide. Therefore, of the acid initially present as thorium chloride (= 40 c.c., expressed in terms of  $N/10$ -acid), 26.2 c.c. had been replaced by hydroxide and 13.8 c.c. by tartrate, and consequently the simplest formula of the basic thorium complex in the solution is





which happens to be also that of the precipitated basic tartrate. If it be assumed that 26.2 c.c. of  $N/10$ -tartaric acid were liberated during the interaction of 40 c.c. of  $N/10$ -sodium tartrate and 100 c.c. of  $M/100$ -thorium chloride, the concentration of the tartaric acid in the 140 c.c. of solution was  $9.33 \times 10^{-3}$ , and  $K_1$  of tartaric acid being taken as  $1 \times 10^{-3}$  (the effect of  $K_2$  is negligible—see J., 1925, 127, 1899), the  $p_H$  was 2.51. A solution (140 c.c.) of tartaric acid of this concentration was found, by means of the hydrogen electrode, to have exactly this  $p_H$ . The solution was titrated electrometrically with  $N/10$ -sodium tartrate; the titration curve, beginning at 40 c.c., is represented by the broken line lying a little below the thorium curve (Fig. 4). The differences in hydrogen-ion concentration shown in the two curves may be due to some interaction between the basic tartrate and the tartaric acid while the former is dissolving.

These solutions did not yield precipitates when treated with alkalis. Non-precipitable solutions could also be prepared by using less sodium tartrate. From the solutions employed in the titrations alkalis produced complete precipitation if 1 mol. or less of either tartaric acid or sodium tartrate had been added for each mol. of thorium chloride. Although  $1\frac{1}{2}$  mols. of sodium tartrate produced a precipitate, this dissolved on addition of alkali and the solution became non-precipitable. Basic thorium tartrate, as was the case with the zirconium precipitate, required a considerable excess of tartaric acid to redissolve it, and the basic complex in the acid solution appeared to be the same as that in the sodium tartrate solution.

Rosenheim, Sammtner, and Davidsohn (*Z. anorg. Chem.*, 1903, 35, 424), in their investigation on complex thorium tartrates, isolated what they regarded as two series of salts containing the thorium in the anion, viz.,  $R_2[ThOT_2]$  and  $R_2[ThO_2T]$ , where  $R = K, Na, \text{ or } NH_4$ . Some of the products are described as "crusts." They attempted to ascertain which of these two salts existed in solution by determining the proportions of thorium nitrate, tartaric acid, and alkali which produced the maximum optical activity. These were stated to be  $Th(NO_3)_4 : 2H_2T : 6ROH$ , and therefore the authors concluded that the salt  $R_2[ThOT_2]$  was indicated. On recalculation, however, these proportions are found to be in error, approximately 1 mol. of tartaric acid having been required instead of the 2 mols. stated, and the amount of alkali ranging from 5 to 7 mols. These are roughly the proportions required in the formation of 1 mol. of thorium hydroxide and 1 mol. of alkali-metal tartrate (compare the series  $R_2[ThO_2T]$ , i.e.,  $R_2T$  and  $ThO_2$ ). The data of those authors show that such a solution was on the point of precipitation, for when the amount of thorium nitrate was increased in the ratio 8 : 7,

a precipitate appeared. As stated above, solutions of thorium chloride and sodium tartrate in equimolecular proportions fail to give a complex solution.

The amounts of  $N/10$ -sodium hydroxide required to neutralise the acid in these complex thorium tartrate solutions, when boiling, were a little greater than those required when the solutions were cold. Whatever the amount of  $N/10$ -sodium tartrate that had been added to 100 c.c. of  $M/100$ -thorium chloride, approximately 35 c.c. of  $N/10$ -sodium hydroxide were required to neutralise the boiling solution, which shows that the basic tartrate complex had slightly hydrolysed to  $\text{ThT}_{0.25}(\text{OH})_{3.5}$ .

The fact that basic thorium tartrate cannot be redissolved by alkali except in the presence of sodium tartrate suggests that sodium tartrate or partly neutralised tartaric acid is responsible for its dissolution. It can scarcely be attributed to the formation of salts of a complex acid, and yet it seems to be due to some reaction taking place between the basic complex and the tartrate ions when present in sufficiently high concentration. A tartaric acid solution, on being gradually neutralised with alkali, therefore acquires a correspondingly increasing solvent capacity for both basic zirconium and basic thorium tartrates.

*Aluminium.*—The curve (Fig. 4) represents the titration of 100 c.c. of  $M/200$ -aluminium sulphate with  $N/10$ -sodium tartrate by means of the hydrogen electrode. Again, an unexpected increase in hydron concentration was shown during the addition of the first 30 c.c. of tartrate solution ( $= 3$  mols.). No precipitate separated and the solution remained clear. Hence, as the sodium tartrate was added, and sodium sulphate thereby formed, a considerable quantity of tartrate ions, instead of combining with the aluminium, was set free to form hydrotartrate ions, some free acid, and a basic aluminium tartrate complex in the solution. The maximum hydron concentration,  $10^{-3.02}$ , was attained when 15 c.c. of sodium tartrate solution had been added. This concentration was probably due mainly to hydrogen ions from the first-stage dissociation of the tartaric acid, the hydrotartrate ions having reacted with the aluminium hydroxide.

Titration were made of the acid liberated in the solutions obtained by adding various quantities of  $N/10$ -sodium tartrate to 100 c.c. of  $M/200$ -aluminium sulphate. Ten c.c. of sodium tartrate were insufficient to produce a solution non-precipitable by alkali, but when 20 c.c. [i.e., 2 mols.  $\text{Na}_2\text{T}$  for 1 mol.  $\text{Al}_2(\text{SO}_4)_3$ ] or more were used, the solutions became non-precipitable and the amounts of alkali required to produce neutrality to phenolphthalein varied from 2.4 to 2.7 equivalents (for 1Al). In the boiling solutions, 2.8 equivalents

produced neutrality in each case. Therefore both in cold and in hot solutions a little tartrate remained firmly bound to the aluminium hydroxide. These experiments again seem to show that the non-precipitability is due to the existence of stable basic tartrates, the compositions of which, in the solutions studied, varied from  $\text{AlT}_{0.3}(\text{OH})_{2.4}$  to  $\text{AlT}_{0.1}(\text{OH})_{2.8}$ .

*Beryllium*.—A small diminution in the hydrogen-ion concentration occurred in the titration of 100 c.c. of  $M/40$ -beryllium sulphate with  $N/10$ -sodium tartrate. This was not due to the formation of a less hydrolysed beryllium tartrate, for, as is shown by the curve (Fig. 4), no distinct change in hydrogen-ion concentration occurred when the requisite amount of sodium tartrate (50 c.c.) had been added. The small variation in the hydron concentration was caused by equilibria set up between the added tartrate ions and the hydrotartrate ions, which, by failing to react with the beryllium, left it in the solution in the form of a basic tartrate. The high concentration of hydrotartrate ions was evidently due to their incapacity to react with that part of the beryllium hydroxide which gives rise to "soluble basic salts."

Solutions which contained one or more mols. of beryllium sulphate to one of sodium tartrate were completely precipitated by alkali, although solutions containing the reactants in the molar ratio 1 : 2 did not yield precipitates. The amounts of titratable acid in the complex tartrate solutions were approximately 1.53 equivalents for each molecule of beryllium sulphate taken, and consequently the composition of the final basic complex may be expressed by the formula  $\text{BeT}_{0.24}(\text{OH})_{1.53}$ .

Rosenheim and Woge (*Z. anorg. Chem.*, 1897, **15**, 283) and Rosenheim and Itzig (*Ber.*, 1899, **32**, 3424) isolated two series of complex beryllium tartrates having the general formulæ  $\text{R}_2[\text{Be}_4\text{O}_3\text{T}_2]$  and  $\text{R}_2[\text{Be}_2\text{OT}_2]$ , where  $\text{R} = \text{K}, \text{Na}, \text{or } \text{NH}_4$ . The individuality of these salts is questionable. Salts of the former series were obtained by evaporating hydrogen tartrate salt solutions, saturated with beryllium hydroxide, to syrups and allowing these to solidify, whereas salts of the latter series were prepared in the same way with the one exception that the calculated quantities of beryllium hydroxide were used. The salts were either glassy masses or microcrystalline crusts. Complex salts of the first type cannot give rise to non-precipitability, for, as Rosenheim and Woge state, ammonia produces a precipitate. As already mentioned, solutions containing beryllium sulphate and sodium tartrate in the molar ratio 2 : 1, which is that in  $\text{R}_2[\text{Be}_4\text{O}_3\text{T}_2]$ , are precipitable by alkalis. The latter workers have established, by means of the polarimetric method also used in the case of complex thorium tartrate solutions, that the important complex salt in the

solution was this particular compound,  $\text{Na}_2[\text{Be}_4\text{O}_3\text{T}_2]$ , from a study of solutions containing mixtures of beryllium sulphate, tartaric acid, and sodium hydroxide. The fact that the products which Rosenheim and Woge obtained by saturating solutions of acid salts with beryllium hydroxide should have corresponded to the formula  $\text{R}_2[\text{Be}_4\text{O}_3\text{T}_2]$  is of interest in that the products may be considered as being made up of the neutral tartrate,  $\text{R}_2\text{T}$ , and the basic tartrate,  $\text{Be}_4\text{O}_3\text{T}_2$ , or  $\text{BeT}_{0.25}(\text{OH})_{1.5}$ , which happens to be almost that suggested by these experiments to be present in the complex solutions.

*Chromium.*—The curve (Fig. 4) represents the hydron concentration changes which occurred during the titration of 100 c.c. of  $M/100$ -chrome alum with  $N/10$ -sodium tartrate. The hydron concentrations indicate that the amount of hydrotartrate ions liberated was less than that in the case of the corresponding beryllium titration. The difference appears to be accounted for by the fact that, although the precipitation  $p_{\text{H}}$ , 5.69, of beryllium hydroxide is a little higher than that of chromium hydroxide, 5.34, one-half of the beryllium hydroxide molecule is associated with the formation of soluble basic salts as compared with one-third in the case of chromium, and consequently a larger equivalent amount of acid is rendered available for reaction. The sodium tartrate caused the violet chromium salt solution to turn green.

The formation of complex chromium tartrate solutions which are not precipitable by alkali depends not so much on the amount of sodium tartrate added as on the treatment to which the solutions have been subjected, and in this respect appears to be similar to that of complex oxalate solutions. There is, however, the one difference that whereas oxalate solutions, on prolonged boiling with alkali, yield a precipitate, those of chromium tartrate in general do not. Chromium tartrate solutions, on boiling, become purplish-red, but if they are now treated with alkali at room temperature they turn green as soon as the precipitation  $p_{\text{H}}$  of the hydroxide is reached. As in the case of oxalate solutions, boiling caused the liberation of acid and the simultaneous formation of inert basic salt.

*Zinc.*—The curve (Fig. 4) is that of the titration of 100 c.c. of  $M/50$ -zinc sulphate with  $N/10$ -sodium tartrate. Although the sodium tartrate did not precipitate zinc hydroxide, the hydron concentration on addition of the first 40 c.c. (when the molecular ratio was  $\text{Na}_2\text{T} : \text{ZnSO}_4$ ) was reduced to nearly the precipitation  $p_{\text{H}}$ , 5.2, of zinc hydroxide. Titrations were made with sodium hydroxide and phenolphthalein of the acid liberated when varying quantities of  $N/10$ -sodium tartrate were added to 100 c.c. of  $M/50$ -zinc sulphate; the results are in Table V, where  $a$  = mols. of sodium tartrate per

mol. of zinc sulphate, and  $b$  and  $c$  = equivs. of sodium hydroxide required to produce a precipitate and neutrality, respectively.

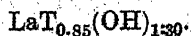
TABLE V.

$a$ .....	2	2.5	3	4	5
$b$ .....	0.41	1.00	—	—	—
$c$ .....	1.14	1.13	1.19	1.14	1.03

The table shows that the minimum quantity of sodium tartrate required to prevent precipitation by alkali was 3 mols. for 1 mol. of zinc sulphate (= 120 c.c.). This quantity is much greater than those required in the case of the weaker bases. Moreover, all the solutions referred to in the table gave a precipitate when boiled with alkali. The change in hydrion concentration after 40 c.c. of sodium tartrate solution had been added shows that not all the hydrions of the tartaric acid had reacted, and the amounts of alkali required to neutralise the acid which had failed to react indicate that the compositions of the basic tartrates in the complex solutions varied from  $\text{ZnT}_{0.49}(\text{OH})_{1.03}$  to  $\text{ZnT}_{0.41}(\text{OH})_{1.19}$ .

*Lanthanum.*—When sodium tartrate was added to a lanthanum nitrate solution, a white, flocculent precipitate formed at  $p_{\text{H}}$  between 6 and 7 [Found in the air-dried precipitate:  $\text{La}_2\text{O}_3$ , 34.6; C (by "wet" combustion), 15.5.  $\text{La}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 12\text{H}_2\text{O}$  requires  $\text{La}_2\text{O}_3$ , 34.75; C, 15.4%]. Czudnowicz (*J. pr. Chem.*, 1860, 79, 39) and Holmberg (*Z. anorg. Chem.*, 1907, 53, 87) prepared this salt, but based their formulæ on the lanthana content only, and reported that the water corresponded to  $9\text{H}_2\text{O}$ . Clève (*Bull. Soc. chim.*, 1874, 21, 202) stated that the water content of the salt dried in a desiccator was  $3\text{H}_2\text{O}$ .

Lanthanum tartrate, although insoluble in water (Rimbach and Schubert, *Z. physikal. Chem.*, 1909, 67, 192), is so readily soluble in mineral acids that when tartaric acid is added to a solution of a lanthanum salt of a strong acid no precipitate is formed; but one is obtained from a solution of lanthanum acetate. It is also readily soluble in alkalis and dissolves in an excess of sodium tartrate or tartaric acid solution. The following experiments were made to ascertain something of its nature in solution. Lanthanum tartrate was precipitated on addition of 30 c.c. of  $N/10$ -sodium tartrate to 30 c.c. of  $N/10$ -lanthanum nitrate. The solution became alkaline to thymol-blue on addition of 11.2 c.c. of  $N/10$ -sodium hydroxide, and the precipitate completely dissolved on addition of 13 c.c. The amount of alkali required for re-solution shows, if it be assumed that the alkali had been converted into sodium tartrate, that the lanthanum had passed back into solution as a basic tartrate,



In another experiment, 50 c.c. of  $N/10$ -sodium tartrate were added to 30 c.c. of  $N/10$ -lanthanum nitrate, and the solution containing the suspended precipitate was titrated, by means of the hydrogen electrode, with  $N/10$ -sodium hydroxide. The precipitate dissolved at  $p_H$  7.9, when 12 c.c. of alkali had been added, the soluble basic tartrate then being  $LaT_{0.90}(OH)_{1.20}$ , but the inflexion indicating the attainment of marked alkalinity did not occur until 14.4 c.c. had been added, and therefore the soluble basic lanthanum tartrate had become slightly decomposed to  $LaT_{0.78}(OH)_{1.44}$ . The curve obtained on adding more alkali showed that the basic tartrate was undergoing further decomposition. The following experiment gives some idea of the extent of the decomposition which takes place in alkaline solutions. Lanthanum tartrate (0.1960 g.) was shaken mechanically with 100 c.c. of 0.014*N*-sodium hydroxide for 24 hours; all the tartrate had then dissolved. The solution was titrated by means of the hydrogen electrode with  $N/10$ -hydrochloric acid, and the excess of free alkali was equivalent to 6.35 c.c. of the acid. The lanthanum tartrate therefore existed in the alkaline solution as  $LaT_{0.59}(OH)_{1.82}$ , and was much more basic than those mentioned above. In this titration, the basic lanthanum tartrate began to be precipitated when the free alkali had just been neutralised, and the  $p_H$  then attained was that required for the precipitation of lanthanum hydroxide.

#### *Discussion.*

The foregoing investigations show that complex tartrate solutions are essentially basic in nature. This is especially evident in the cases of the complex zirconium and thorium tartrate solutions produced by the re-solution, probably without change in composition, of the basic tartrates first precipitated. Unlike the complex solutions which were sometimes formed with acetates and oxalates, those of the tartrates are extremely stable. The basic tartrates, like the basic aggregates in solution, are strongly resistant to alkalis, which probably explains their non-precipitability by such means.

The existence of these basic tartrate complexes would also account for the properties of Fehling's solution. The fact that the ease of reduction to cuprous oxide is comparable with that of freshly precipitated cupric hydroxide suggests that the condition of the cupric salt in alkaline tartrate solutions is in some way related to that of cupric hydroxide itself, as would obtain in basic tartrate complexes.

The condition of copper tartrate on passing into these complex alkaline tartrate solutions is, at any rate, basic. For example, Kahlenberg (*Z. physikal. Chem.*, 1895, **17**, 586), Masson and Steele (*J.*, 1899, **75**, 725), and Pickering (*J.*, 1911, **99**, 169) found that the quantity of sodium or potassium hydroxide necessary to produce

alkalinity in a solution of copper tartrate varied from 1.25 to 1.36 mols., and therefore the basic complexes in the solutions must have varied from  $\text{CuT}_{0.38}(\text{OH})_{1.25}$  to  $\text{CuT}_{0.32}(\text{OH})_{1.36}$ .

Previous workers attempted to account for the anomalies of complex tartrate solutions by regarding the heavy metal as being present in a complex anion. Masson and Steele obtained a substance,  $\text{K}_3\text{Cu}_4\text{C}_{12}\text{H}_7\text{O}_{18}\cdot 5\text{H}_2\text{O}$ , by precipitation with alcohol from a copper tartrate solution which had been neutralised with 1.25 equivalents of potassium hydroxide. The substance, which was isolated as a dark blue, gummy mass (and therefore was of questionable character), was in effect composed of  $3\text{K}_2\text{T}$  and  $8\text{CuT}_{0.375}(\text{OH})_{1.25}$  and was probably a mixture of potassium tartrate with a preponderance of basic copper tartrate. Their migration experiments on solutions of this substance are important in that they show that some copper had passed into the portion carrying the negative charge, but this may have been due equally well to the colloidal nature of the basic copper tartrate as to the presence of a complex copper anion. Pickering also obtained flocculent precipitates from copper tartrate solutions by adding alcohol. The unwashed precipitates (whose constitutions he tried to establish by regarding some of the copper as quadrivalent) contained variable quantities of potassium salt, all of which, together with some copper, could be removed by washing. Wark (J., 1923, 123, 1815, 1826; 1924, 125, 2004) has suggested that the complexity of solutions containing copper and malic acid is due to the formation of cuprimalic acid,  $\text{HCuC}_4\text{H}_3\text{O}_5$ , isomeric with the normal cupric malate.

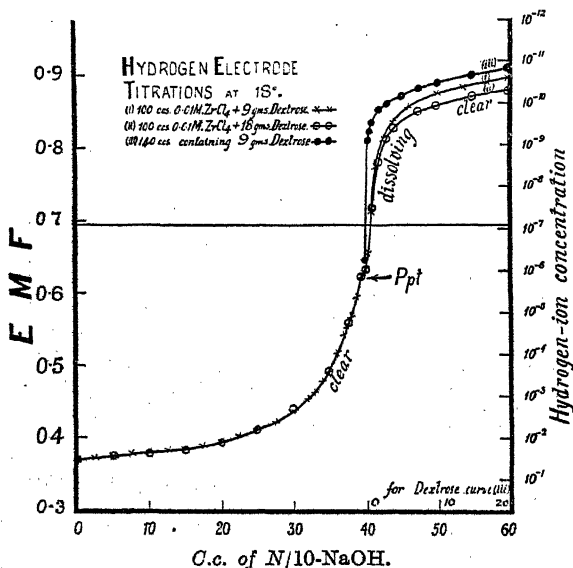
The formation of the complex tartrate solutions of zirconium and thorium by the re-solution of the basic precipitates seems to have been due to the sodium tartrate which was present, although it has not been possible to associate any precise quantity of the latter with that of the respective basic tartrates. Many attempts have been made to account for the complexity of tartrate solutions by assuming that their formation involves reactions with the hydrogen atoms of the hydroxy-groups. It is difficult, however, to imagine that zirconium hydroxide, for example, one of the weakest bases, should be capable of so reacting, when strong bases show so very little aptitude. If the hydroxy-groups of tartaric acid are weakly acidic (their acidity is so small that it is not measurable by any physical method), they might be able to react with metallic bases, provided that the products formed were insoluble and therefore were removed from the sphere of action. Such a condition would probably be satisfied if the bases which had combined passed into the dispersed particles of a colloidal solution.

Many hydroxy-compounds, such as the sugars and glycerol, have

a definite, though very slight, acid character (compare Michaelis and Rona, *Biochem. Z.*, 1913, **49**, 248) and their dissociation constants can be measured. The dissociation constant of glycerol as a monobasic acid at  $17.5^\circ$  is  $7 \times 10^{-15}$ , and, in fact, the presence of glycerol in an alkali solution has a barely measurable effect on the  $p_H$ . Yet its effect on a zirconium chloride or ferric chloride solution may be such that alkalis fail to precipitate the hydroxide.

The reaction which must take place between the glycerol and the metallic base provides an explanation of the well-known protective action on ferric oxide hydrosols prepared by dialysis of ferric

Fig. 5.



chloride-glycerol solutions. It is significant, too, that the hydrosols so prepared are clear in transmitted light. The glycerol may retard the growth of the colloidal particles.

If the behaviour of the hydroxy-groups of tartaric and other hydroxy-acids is due to their feebly acid character, then it seems that complex tartrate solutions are essentially protected colloidal solutions. The following electrometric titrations were carried out to test this view. Michaelis and Rona (*loc. cit.*) having shown that dextrose is a stronger acid ( $K = 6.6 \times 10^{-13}$ ; compare Britton, J., 1925, **127**, 1902) than glycerol, it was decided to use the former in the titrations. A solution (100 c.c.),  $M/100$  with respect to zirconium chloride and  $M/2$  with respect to dextrose (9 g. in 100 c.c.), was titrated with  $N/10$ -sodium hydroxide at  $18^\circ$  by means of the



hydrogen and the normal calomel electrode. The curve is shown in Fig. 5, the points obtained being marked by crosses. A very slight opalescence was produced by 38.5 c.c. of the alkali ( $p_H = 5.22$ ), and a precipitate by 39.5 c.c. ( $p_H = 5.89$ ). This began to dissolve when 40 c.c. (*i.e.*, 4NaOH : ZrCl<sub>4</sub>) had been added, and the solution was cleared by 50 c.c. In the titration of zirconium chloride solution alone (J., 1925, 127, 2125), the solution first became visibly colloidal with 1.5 equivalents of alkali ( $p_H = 1.86$ ), but in the present titration the effect of the dextrose was manifested in the delay of precipitation until nearly the whole of the alkali required to convert the zirconium chloride into the hydroxide had been added and the hydrogen-ion concentration had become extremely small, *viz.*,  $10^{-6}$ . The fact that the solution remained clear until 3.85 equivalents of alkali had been added suggests that, although the dextrose was incapable of influencing the hydrogen-ion concentration of the solution, it had the effect of repressing the growth of the basic particles below the limit necessary to produce visible colloidalty. Table VI, compiled from the observed voltages, shows that during the addition of the first 40 c.c. of alkali the zirconium chloride was more basic than ZrCl(OH)<sub>3</sub>. The ionisation of dextrose is much too small to affect the hydrogen-ion concentrations of solutions whose  $p_H$  is less than 6, and consequently the hydron concentrations of the basic zirconium chloride solutions have been regarded as coming entirely from the hydrolysed acid.

TABLE VI.

C.c. of N/10- NaOH.	E.M.F.	% Hydrolysis of un- neutralised part.	Atoms of Cl in ZrCl <sub>4</sub> neutralised.	Composition of basic zirconium chloride. Atoms per 1Zr.		Mols. of free HCl referred to 1Zr.
				Cl.	OH.	
0.0	0.370	77.8	0	0.89	3.11	3.11
5.0	0.374	79.5	0.5	0.78	3.22	2.72
10.0	0.379	79.8	1.0	0.61	3.39	2.39
15.0	0.386	75.7	1.5	0.61	3.39	1.89
20.0	0.395	68.7	2.0	0.63	3.37	1.37
25.0	0.413	46.5	2.5	0.80	3.20	0.70
30.0	0.438	26.8	3.0	0.73	3.27	0.27
35.0	0.491	6.7	3.5	0.47	3.53	0.03
37.5	0.552	1.2	3.75	0.25	3.75	0.003
38.0	0.566	1.1	3.8	0.20	3.80	0.002
39.0	0.598	0.5	3.9	0.10	3.90	0.0005
39.5	0.623	0.4	3.95	0.05	3.95	0.0002
40.0	0.634	0	4	0	4	0

The last column shows that when the solution began to opalesce, with 38.5 c.c. of alkali, the amount of free acid had become negligible. It is remarkable that the dextrose was able to maintain the highly basic zirconium chloride (columns 5 and 6) in a solution which was quite clear. Borax and sodium carbonate also delay precipitation

by alkali until somewhat more than 3 equivalents have been added (this vol., p. 125).

In order to ascertain whether the dextrose had entered into any reaction which might have influenced the  $p_H$  of the solution during the re-solution of the zirconium hydroxide in the sodium hydroxide, a solution of 140 c.c. (i.e., the volume of the titrated solution when the stoichiometrical amount of alkali had been added) containing 9 g. of dextrose was titrated with  $N/10$ -sodium hydroxide. The data and dissociation constant figures of dextrose as a monobasic acid are given in a previous paper (J., 1925, **127**, 1902). In Fig. 5 the titration curve is the one beginning at 40 c.c. of  $N/10$ -sodium hydroxide given at the top of the diagram. By comparing the two curves, it will be seen that the presence of the zirconium hydroxide in the one solution caused a perceptible diminution in  $p_H$ , and consequently the hydroxide on dissolution must have combined in some way with the dextrose. It is difficult to understand how the zirconium hydroxide effected this increase in hydrogen-ion concentration. Had it reacted simply with the dextrose to form inert colloidal aggregates, this, in effect, would have been equivalent to the removal of some dextrose from the solution and therefore would have given rise to a diminished hydron concentration. An increased hydrogen-ion concentration seems to be possible only by assuming that the zirconium hydroxide had, in combining with the dextrose, given rise to a complex acid slightly stronger than dextrose itself. All that the titration can be said to show is that dextrose does enter into some kind of reaction with the zirconium hydroxide in effecting its dissolution in alkali solutions.

A second titration was that of 100 c.c. of  $M/100$ -zirconium chloride and  $M/1$ -dextrose solution (18 g. in 100 c.c.). The increased amount of dextrose was without further effect during the addition of the first 40 c.c. of alkali, but tended to cause a more rapid re-solution of the zirconium hydroxide as the excess of alkali was added. The data for this curve are indicated by circles in Fig. 5.

### *Summary.*

(1) Sodium acetate at the ordinary temperature fails to precipitate weak bases, although the precipitation  $p_H$ 's of the respective hydroxides may be exceeded. An exception is the reaction with thorium sulphate solution. There is good evidence that weak metallic bases exist in complex acetate solutions as basic acetates.

(2) Sodium oxalate produces a basic precipitate from zirconium chloride solution through the incapacity of the hydrions from the second stage of dissociation of oxalic acid to react with zirconium hydroxide, but the precipitate dissolves in excess of the reagent.

The oxalate does not produce precipitates from solutions of salts of slightly stronger bases, *e.g.*, aluminium and chromium hydroxides, even although it is probable that very little reaction can take place between them and the hydro-oxalate ions. Observations on solutions of chromium hydroxide in oxalic acid and of potassium chromium oxalate suggest that both their properties and the existence of the series  $3R_2C_2O_4, Cr_2(C_2O_4)_3$  arise from the nature of the reactants.

(3) The reaction of sodium tartrate with salts of thorium and aluminium in solution is remarkable in that increased hydron concentrations are at first produced; in the case of thorium, a basic tartrate precipitate is formed, even although the hydron concentration is considerably higher than that necessary for the precipitation of the hydroxide.

(4) Hydrogen electrode titrations of zirconium chloride solutions containing dextrose with sodium hydroxide show that some reaction must take place between the zirconia and the hydroxy-groups of dextrose.

The author desires to express his thanks to the Department of Scientific and Industrial Research for a personal grant, to the Chemical Society for a grant from its Research Fund for the purchase of salts of the rarer metals, and to Professor J. C. Philip, F.R.S., for kindly placing facilities at his disposal.

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### XXXIX.—*The Absorption of Gases by Colloidal Solutions.*

By ALOIS GATTERER.

ONE of the most important studies of colloid chemistry is that dealing with adsorption and absorption in colloidal solutions, for not only is it of considerable practical value, but also it may throw light on the structure of the colloids themselves. The study of gaseous absorption in particular may be expected to yield definite and valuable results because of the chemical and electrical neutrality of solvent and solute. Of the few investigations of this kind that have hitherto been made, those of Geffcken (*Z. physikal. Chem.*, 1904, **49**, 297) and Findlay and his co-workers (*J.*, 1910, **97**, 536; 1912, **101**, 1459; 1913, **103**, 636; 1914, **105**, 291) are limited in their scope, being confined to comparatively few gases and solutions, to low concentrations and, above all, to one temperature, *viz.*, 25°.

Consequently, our knowledge of the absorptive power of colloidal

solutions is meagre and does not furnish a sufficiently broad experimental foundation for a trustworthy theory. A wide investigation of absorption has therefore been undertaken, with various colloidal solutions and at temperatures ranging from 5° to 25°. The colloidal solutions have been characterised by determinations not only of density and concentration but also of electrical conductivity, viscosity, the Tyndall effect, and absorption of light, for only in this way is it possible to define these complex systems so precisely that they can be exactly reproduced.

The observations here recorded refer only to two gases, carbon dioxide and acetylene, and to two colloidal solutions, ferri ferrocyanoide and ferric hydroxide; the former were chosen because of their acidic and neutral character respectively, and the latter because they are, respectively, positive and negative colloids.

#### EXPERIMENTAL.

*Preparation of Solutions.—Ferri ferrocyanoide.* The solution was prepared according to Zsigmondy ("Kolloid Chemie," 1920, 3rd ed., p. 500) by mixing 2*N*-solutions of sodium ferrocyanoide and ferric chloride. The precipitate was carefully washed, redissolved in a small quantity of the ferrocyanoide, and the solution was concentrated by heating in a vacuum. The maximum concentration obtained was about 8%.

*Ferric hydroxide.* A solution of pure ferric hydroxide in acetic acid was diluted and, after the method of Péan de St. Gilles, boiled until the ratio of acetic acid to ferric hydroxide became 1 : 30—1 : 60. The solution was then evaporated, not under atmospheric pressure, but under reduced pressure, whereby a much higher degree of dispersion, as shown by the Tyndall effect (compare Figs. 1 and 2), was obtained. This more highly dispersed solution appears to be intermediate between the solution of Graham and that of P. de St. Gilles.

*Preparation of Gases.—*The carbon dioxide was carefully washed and its purity was confirmed by the value obtained for its solubility in distilled water. Acetylene was generated from calcium carbide and freed from impurities by treatment with chromic acid and potassium hydroxide and by absorption in acetone. Analyses of the purified product by means of ammoniacal cuprous chloride showed residues of 0, 2, and 3 c.c. in 100 c.c.

*Apparatus and Outline of Method.—*The method of Ostwald was employed to measure absorption (Ostwald-Luther, "Handbuch der Physicochemischen Messungen," 1910, 3rd ed., p. 246). The solutions were freed from air by boiling in a vacuum and, without contact with air, transferred to the vacuum mixing vessel at 25°.

The gases were saturated with water vapour at the same temperature. Five measurements were made with a given solution at five different temperatures, the process being repeated after an interval of several hours to check the former results. The calculation of the solubility is based on the formula (see Ostwald-Luther, *op. cit.*)

$$l = \left[ V_{b_1} \frac{T_a(b_1 - h_{b_1})}{T_{b_1}(b_1 - h_a)} - V_{b_2} \frac{T_a(b_2 - h_{b_2})}{T_{b_2}(b_2 - h_a)} - V_a \right] \frac{1}{V_f},$$

where  $l$  = Ostwald's solubility;  $V_{b_1}$  = initial volume of gas in the burette at temperature  $T$  (abs.) and pressure  $b_1$ ;  $V_{b_2}$  = final volume of gas in the burette;  $T_a$  = absolute temperature of the thermostat;  $T_{b_1}$  and  $T_{b_2}$  = initial and final temperature, respectively, of gas in burette;  $b_1$  and  $b_2$  = pressure of the atmosphere at commencement and end of experiment;  $h_a$ ,  $h_{b_1}$ , and  $h_{b_2}$  = tension of water vapour at  $T_a$ ,  $T_{b_1}$ , and  $T_{b_2}$ , respectively;  $V_a$  = volume of liquid withdrawn, measured at  $T_a$ ;  $V_f = V - V_a$  = volume of liquid contained in the absorption vessel; and  $V$  = volume of the absorption vessel at temperature  $T_a$ .

The changes in volume of the solutions and of the mixing vessel at various temperatures were taken into consideration. The probable error was  $\pm 0.4\%$ . In certain cases, owing to an exceedingly slow rate of absorption, the completion of this was not reached, and this may be the explanation of the lack of smoothness in some of the curves. The values of  $l$  are given either in percentages, *i.e.*, number of grams in 100 c.c. of solution, or in gram-equivalents. All values of volume are calculated for  $20^\circ$ . Although it is uncertain whether the colloids in question have definite chemical formulæ, yet for the sake of clearness the gram-equivalent of Prussian blue was taken as  $1/12 \text{ Fe}_4[\text{Fe}(\text{CN})_6]_3 = 71.603$ , and that of ferric hydroxide as  $1/3 \text{ Fe}(\text{OH})_3 = 35.621$ .\*

#### *Solubility of Carbon Dioxide in Solutions of Prussian Blue.*

The values in Table I have been obtained by different workers for the solubility of carbon dioxide in water.

Findlay (*loc. cit.*) gives a somewhat lower value, *viz.*, 0.817 at  $25^\circ$ .

The solubility values ( $l$ ) of carbon dioxide in solutions of Prussian blue are in Table II and Fig. 3 (unbroken lines).

\* According to Hofmann ("Lehrbuch der Anorganischen Experimental-chemie," 1918, p. 641) soluble Prussian blue has the formula  $\text{Fe}(\text{CN})_6\text{NaFe}$ . This, of course, would change the above equivalent weight. Hofmann's formula, however, is not generally accepted, and, moreover, does not agree with the author's results. Further, if Hofmann's formula is assumed, the results obtained by the gravimetric and the volumetric methods do not agree.

TABLE I.

T.	Bohr and Bock.*	Geffcken.†	Gatterer.‡			Mean.
	<i>l.</i>	<i>l.</i>	<i>l.</i>			
25°	0.829	0.8255	0.826	0.823	0.830	0.826
20	0.942	—	0.933	0.936	0.940	0.936
15	1.072	1.070	1.066	1.072	1.073	1.070
10	1.238	—	1.233	1.244	1.242	1.240
5	1.449	—	1.440	1.453	1.445	1.446

\* *Wied. Ann.*, 1891, 44, 318. † *Loc. cit.* ‡ In this and the following tables the exact temperatures are: 25.00°, 19.98°, 14.96°, 9.95°, and 4.97° instead of 25°, 20°, 15°, 10°, and 5°, respectively. In the solubility diagrams, the mean values in the tables are represented. For economy in space, the curves of different temperature intervals are moved closer together.

TABLE II.

	25°.	20°.	15°.	10°.	5°.
Soln. 1.	0.8424	0.9510	1.086	1.254	1.451
<i>c</i> = 0.896N	0.8418	0.9515	1.087	1.255	1.454
	<i>0.8421</i>	<i>0.9512</i>	<i>1.087</i>	<i>1.255</i>	<i>1.453</i>
Soln. 2.	0.8516	0.9617	1.095	1.262	1.463
<i>c</i> = 0.51N	0.8494	0.9610	1.092	1.265	1.466
	<i>0.8505</i>	<i>0.9613</i>	<i>1.093</i>	<i>1.264</i>	<i>1.464</i>
Soln. 3.	0.8566	0.9696	1.105	1.276	1.477
<i>c</i> = 0.37N	0.8588	0.9672	1.106	1.279	1.479
	<i>0.8577</i>	<i>0.9684</i>	<i>1.106</i>	<i>1.277</i>	<i>1.478</i>
Soln. 5.	0.8544	0.9653	1.100	1.270	1.472
<i>c</i> = 0.178N	0.8517	0.9613	1.096	1.267	1.472
	<i>0.8530</i>	<i>0.9633</i>	<i>1.093</i>	<i>1.268</i>	<i>1.472</i>
Soln. 4.	0.8430	0.9510	1.0850	1.254	1.463
<i>c</i> = 0.126N	0.8456	0.9568	1.092	1.263	1.469
	<i>0.8443</i>	<i>0.9549</i>	<i>1.089</i>	<i>1.258</i>	<i>1.465</i>

Mean values are printed in italics in all the tables.

The temperature coefficients of absorption of carbon dioxide in solutions of Prussian blue ( $\Delta l/\Delta t$ ) are in Table III, and have been calculated from the results in Table II.

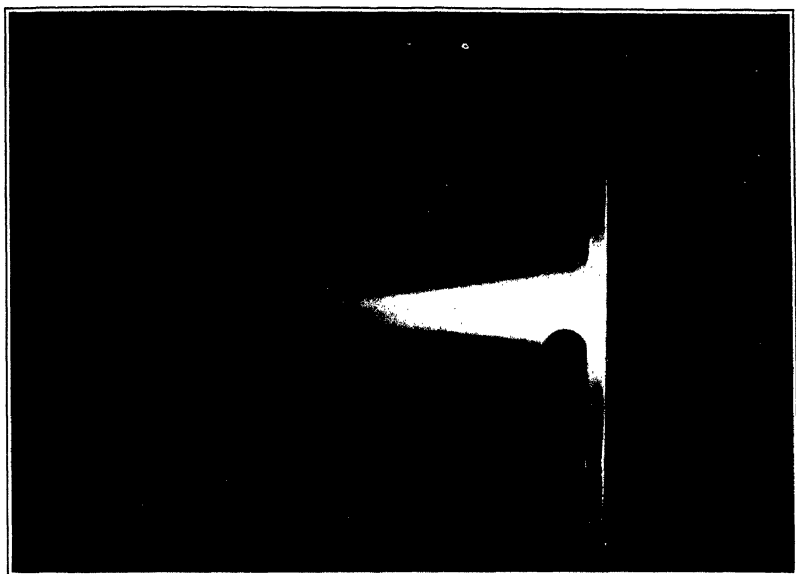
TABLE III.

Soln.	25—20°.	20—15°.	15—10°.	10—5°.
1	0.0218	0.0271	0.0336	0.0396
2	0.0221	0.0264	0.0342	0.0400
3	0.0221	0.0274	0.0342	0.0402
5	0.0221	0.0268	0.0340	0.0408
4	0.0219	0.0268	0.0338	0.0414
H <sub>2</sub> O	0.0220	0.0268	0.0340	0.0412

#### *Solubility of Carbon Dioxide in Solutions of Ferric Hydroxide.*

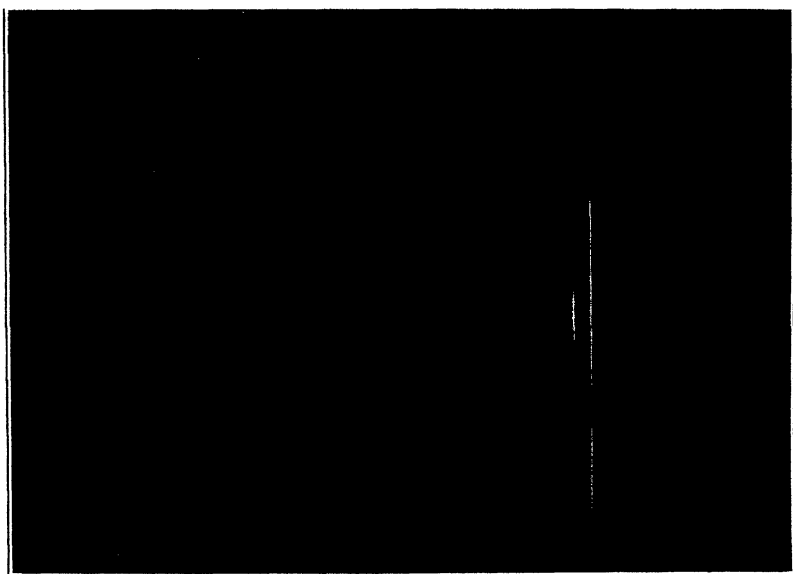
In Table IV and Fig. 3 (broken lines) are the solubilities of carbon dioxide in solutions of ferric hydroxide at temperatures ranging from 5° to 25° in intervals of 5°, whilst in Table V are the temperature coefficients ( $\Delta l/\Delta t$ ).

FIG. 1.



*Tyndall effect for solution evaporated under atmospheric pressure.*

FIG. 2.



*Tyndall effect for solution evaporated in a vacuum.*

[To face p. 302.]





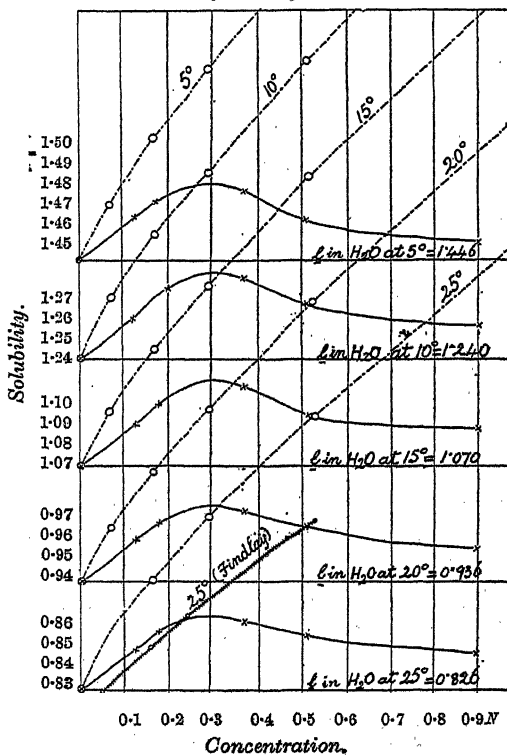
TABLE IV.

	25°.	20°.	15°.	10°.	5°.
Soln. 2.	0.8618	0.9601	1.093	1.264	1.467
$c = 0.071N$	0.8547	0.9619	1.098	1.271	1.476
	0.8533	0.9610	1.095	1.267	1.471
Soln. 1.	0.8788	0.9906	1.127	1.300	1.509
$c = 0.144N$	0.8740	0.9834	1.119	1.297	1.498
	0.8764	0.9870	1.123	1.297	1.503
Soln. 4.	0.9073	1.017	1.155	1.326	1.536
$c = 0.293N$	0.9053	1.016	1.153	1.326	1.533
	0.9063	1.016	1.154	1.326	1.534
Soln. 3.	0.9531	1.067	1.203	1.379	1.583
$c = 0.513N^*$	0.9521	1.066	1.205	1.380	1.585
	0.9526	1.066	1.204	1.379	1.584
Soln. 5.	1.030	1.146	1.287	1.467	—
$c = 0.967N$	1.035	1.152	1.295	1.473	1.684
	1.032	1.149	1.291	1.470	1.680

\* This value was obtained from a density determination.

FIG. 3.

Solubility of carbon dioxide in solutions of Prussian blue and ferric hydroxide.



---  $\text{CO}_2$  in  $\text{Fe}(\text{OH})_3$ . —  $\text{CO}_2$  in  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

TABLE V.

Soln.	25—20°.	20—15°.	15—10°.	10—5°.
2	0.0215	0.0268	0.0344	0.0408
1	0.0221	0.0272	0.0348	0.0412
4	0.0220	0.0276	0.0344	0.0416
3	0.0227	0.0276	0.0350	0.0410
5	0.0234	0.0284	0.0358	0.0420
H <sub>2</sub> O	0.0220	0.0268	0.0340	0.0412

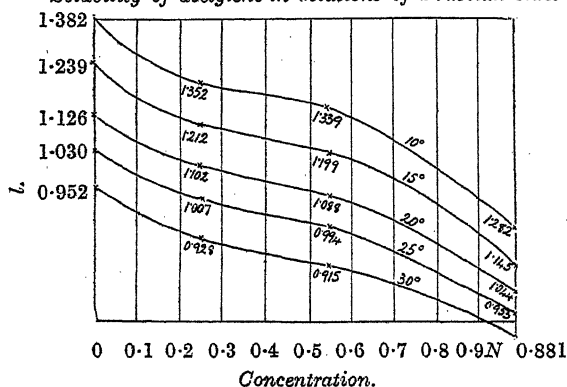
*Solubility of Acetylene in Solutions of Prussian Blue.*

The following solubility values of purified acetylene in distilled water were obtained (Table VI).

TABLE VI.

T.	l.			Mean.
30°	0.951	0.950	0.954	0.952
25	1.030	1.028	1.031	1.030
20	1.126	1.125	1.127	1.126
15	1.239	1.239	1.241	1.239
10	1.381	1.383	1.383	1.382

FIG. 4.

*Solubility of acetylene in solutions of Prussian blue.*

The values of Winkler, according to unpublished communications (Landolt-Börnstein-Roth, "Physikalisch-Chemie Tabellen," 1912, p. 600), are calculated only to the second decimal place and, on the average, are smaller by 1.5—2% than those of the author, as the following figures show :—

	30°.	25°.	20°.	15°.	10°.
Abs. coeff. (Winkler) .....	0.84	0.93	1.03	1.15	1.31
Abs. coeff. from Table VI, mean values .....	0.858	0.944	1.049	1.175	1.330
Diff. % .....	2.1	1.5	1.8	2.1	1.5

Only a more accurate study of Winkler's experiments could determine whether or not this difference is due to impurities in the gas.

Table VII and Fig. 4 show the solubility of acetylene in solutions of Prussian blue, and Table VIII the temperature-coefficients per degree.

TABLE VII.

	30°.	25°.	20°.	15°.	10°.
Soln. II.	0.9286	1.007	1.100	1.210	1.351
$c = 0.250N$	0.9292	1.007	1.103	1.214	1.365
	0.9289	1.007	1.102	1.212	1.358
Soln. I.	0.9186	0.9966	1.089	1.199	1.335
$c = 0.548N$	0.9113	0.9908	1.086	1.199	1.343
	0.9149	0.9937	1.088	1.199	1.339
Soln. III.	0.8808	0.9543	1.042	1.147	1.276
$c = 1.028N$	0.8825	0.9512	1.046	1.142	1.289
	0.8816	0.9527	1.044	1.145	1.282
Soln. IV.					
$c = 0.75N^*$	0.901	0.976	1.071	1.179	1.317

\* This value was obtained from a density determination, and the corresponding values of  $l$  from the graph (Fig. 4).

FIG. 5.

*Solubility of acetylene in solutions of ferric hydroxide.*

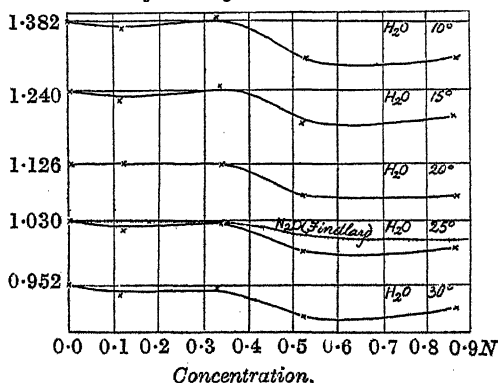


TABLE VIII.

Soln.	30—25°.	25—20°.	20—15°.	15—10°.
II	0.0156	0.0190	0.0220	0.0282
I	0.0158	0.0188	0.0222	0.0280
IV	0.0150	0.0190	0.0216	0.0276
III	0.0142	0.0182	0.0202	0.0274
H <sub>2</sub> O	0.0156	0.0192	0.0226	0.0286

*Solubility of Acetylene in Solutions of Ferric Hydroxide.*

The data are in Table IX and are shown by the curves in Fig. 5 the temperature coefficients are in Table X.

TABLE IX.

	30°.	25°.	20°.	15°.	10°.
Soln. III.	0.9405	1.020	1.109	1.229	1.372
$c = 0.871N$	0.9394	1.016	1.112	1.225	1.366
	0.9400	1.018	1.111	1.227	1.364
Soln. II.	0.9360	1.015	1.111	1.226	1.368
$c = 0.521N$	0.9360	1.016	1.111	1.223	1.361
	0.9360	1.016	1.111	1.224	1.364
Soln. I.	0.9499	1.030	1.126	1.240	1.381
$c = 0.336N$	0.9492	1.028	1.126	1.243	1.386
	0.9495	1.029	1.126	1.241	1.383
Soln. IV.	0.9446	1.025	1.125	1.230	1.380
$c = 0.12N$	0.9426	1.024	1.129	1.233	1.378
	0.9479	1.027	1.123	1.236	1.378
	0.9450	1.026	1.126	1.236*	1.379

\* More probable value.

TABLE X.

Soln.	30—25°.	25—20°.	20—15°.	15—10°.
III	0.0156	0.0186	0.0232	0.0274
II	0.0160	0.0190	0.0226	0.0280
I	0.0153	0.0194	0.0230	0.0284
IV	0.0162	0.0200	0.0220	0.0292
H <sub>2</sub> O	0.0156	0.0192	0.0226	0.0286

*Examination of the Colloidal Solutions.*

In order to define the colloid systems employed and to facilitate re-examination, detailed investigations have been made into the chemical and physical properties of the colloidal solutions used, in the hope that from a consideration of the solubility phenomena and other properties, the intrinsic structures may perhaps be determined. The systems were investigated, therefore, from the point of view of (1) concentration, (2) density, (3) electrical conductivity, (4) depression of the freezing point, and (5) viscosity.

1. *Concentration.*—(a) *Prussian blue.* Gravimetric and volumetric analyses were made. The evaluation of the effective concentration met with some difficulty, owing to a certain quantity of peptising agent which was present in solution. This was avoided in the following way. A certain quantity of solution (5—10 g.) was heated and sodium hydroxide added until all the Prussian blue was converted into ferric hydroxide, which was filtered off. The filtrate was acidified with dilute sulphuric acid, and the sodium ferrocyanide titrated with  $N/10$ -potassium permanganate until the pink colour was permanent. From the quantity of permanganate used, the amount of  $\text{Fe}(\text{CN})_6'''$  ions which remained after the reaction with sodium hydroxide was easily calculated. There were also  $\text{Fe}(\text{CN})_6'''$  ions present from the beginning in the peptised solution, and for this reason the total  $\text{Fe}(\text{CN})_6'''$  found would give too large a

value for the Prussian blue content. To establish the exact quantity of the latter volumetrically, the ratio ( $\phi$ ) of  $\text{Fe}(\text{CN})_6'''$  formed from the Prussian blue to the total  $\text{Fe}(\text{CN})_6'''$  present was determined by gravimetric analysis of the precipitated ferric hydroxide. This was dissolved in dilute hydrochloric acid, re-precipitated with ammonia, and estimated as ferric oxide. The sodium ferrocyanide equivalent to the ferric oxide found was the amount of ferrocyanide obtained from the Prussian blue, which was thus directly determined. The value of  $\phi$  could now be found—using the results with permanganate—and was calculated to be 0.9430. Since  $\phi$  was constant (all solutions being of one preparation), all measurements of the concentration of Prussian blue could then be made by the permanganate method, which was therefore used. Both methods show a satisfactory agreement to within 0.1%, *e.g.*, solution I gave 3.91% volumetrically and 4.02% by the gravimetric method, and solution III, 7.368 and 7.362%, respectively.

(b) *Ferric hydroxide.* The concentration of this solution was determined from the amount of ferric oxide obtained on evaporating a definite quantity of the solution and heating the residue to redness. Considerable difficulty was experienced in determining the quantity of the peptising agent (acetic acid). In the first place, the ratio  $\text{Fe}(\text{OH})_3$ : peptising agent was not constant, because the latter changed whenever the solution was boiled; and secondly, the quantity of acetic acid present was so small that direct titration could afford no exact results. Finally, about 30–40 g. of the solution were acidified with dilute sulphuric acid and about one litre of the resulting solution was distilled. The acetic acid in the distillate was neutralised with baryta, and the excess of this precipitated with carbon dioxide. The whole was concentrated to a small volume, the barium carbonate filtered off, and the barium acetate in the filtrate precipitated with sulphuric acid. The amount of acetic acid was calculated from the weight of barium sulphate found. The greater solubility of barium carbonate over barium sulphate was taken into consideration in the results, which are in Table XII.

2. *Density.*—Densities were determined with a large pycnometer, and the results compared with the density of water at 4° and reduced to vacuum values. Only the results actually obtained are in Tables XI and XII. The results show that, over the whole temperature range studied, density is a linear function of concentration.

3. *Electrical Conductivity.*—The object of these measurements was to determine to what degree the colloid was free from contamination by electrolytes; for an increase in conductivity might have been due to such contamination and eventually to colloidal

TABLE XI.  
Concentration and Density,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

No.	Concentration.		Peptis., $\text{Na}_4[\text{Fe}(\text{CN})_6]$ .		Density.					
	Equiv. N.	%.	Equiv. N.	%.	30°.	25°.	20°.	15°.	10°.	5°.
$\text{H}_2\text{O}^\dagger$	—	—	—	—	0.9957	0.9971	0.9982	0.9991	0.9997	1.0000
2	0.126	0.94	0.008	0.06	—	1.0029*	1.0040	1.0049	1.0054*	1.0059
5	0.178	1.27	0.011	0.08	—	1.0055*	1.0066	1.0075	1.0081*	1.0086
II	0.250	1.788	0.016	0.12	1.0671	1.0085	1.0096*	1.0105	1.0111	—
3	0.37	2.64	0.022	0.17	—	1.0142*	1.0153	1.0162	1.0168*	1.0172
2	0.51	3.65	0.030	0.23	—	1.0213*	1.0224	1.0233*	1.0239	1.0242
I	0.546	3.91	0.033	0.25	1.0205*	1.0219	1.0230*	1.0238	1.0244*	—
I	0.896	6.41	0.053	0.40	—	1.0374*	1.0385	1.0394	1.0401*	1.0404
III	1.028	7.36	0.062	0.47	1.0427*	1.0442	1.0454*	1.0462	1.0467*	—

† Compare Landolt-Börnstein-Röth, *op. cit.*, p. 42.

TABLE XII.  
Concentration and Density,  $\text{Fe}(\text{OH})_3$ .

No.	Concentration.		Peptisation, $\text{CH}_3\text{COOH}$ .		Density.					
	Equiv. N.	%.	Equiv. N.	%.	30°.	25°.	20°.	15°.	10°.	5°.
$\text{H}_2\text{O}^\dagger$	—	—	—	—	0.9957	0.9971	0.9982	0.9991	0.9997	1.0000
2	0.071	0.252	0.002	0.01	—	0.9982	0.9993	1.0002*	1.0008	1.0011
IV	0.12	0.425	—	—	0.9984	0.9998	1.0009	1.0018*	1.0024	—
I	0.144	0.514	0.0036	0.021	—	1.0002*	1.0014	1.0023*	1.0027*	1.0030
4	0.293	1.042	0.003	0.017	—	1.0037*	1.0048	1.0057	1.0063*	1.0066
I	0.336	1.196	—	—	1.0031*	1.0046	1.0057*	1.0066	1.0072*	—
3	0.513†	1.825	0.0096	0.057	—	1.0087*	1.0098	1.0106	1.0112*	1.0115
II	0.521	1.875	—	—	1.0075*	1.0089	1.0100*	1.0109	1.0114*	—
III	0.871	3.103	—	—	1.0157	1.0171	1.0182	1.0191*	1.0197	—
5	0.967	3.446	0.011	0.064	—	1.0191*	1.0202	1.0211	1.0218*	1.0221

† Compare Landolt-Börnstein-Röth, *op. cit.*, p. 42.

‡ This number is obtained from a density determination.

The values marked \* in Tables XI and XII were obtained experimentally, the others by interpolation.

ions. Moreover, the questions arise (1) to what extent is peptisation changed by the action of the colloidal solution, and (2) are ionisation and ionic mobility much the same, at similar concentrations, as in a pure solvent?

The Kohlrausch method, with inductor and telephone, was employed and the results are in the following tables and diagrams.

(a) *Prussian Blue* (see Table XIII and Fig. 6). All measurements were made at 18°. For purposes of comparison the conductivity of pure sodium ferrocyanide is given in Table XIV and shown graphically in Fig. 7.

FIG. 6.

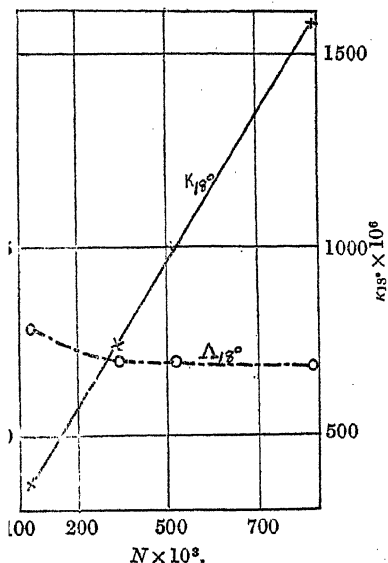
*Prussian blue.*

TABLE XIII.

*Prussian blue.*

Soln.	$N \times 10^3$	$\kappa_{18^\circ} \times 10^6$	$\Lambda_{18^\circ}$
1	896	1575.0	1.75
2	510	992.6	1.94
3	370	750.0	2.03
4	126	359.4	2.85

$$\Lambda = \kappa \times 10^6 / N \times 10^3.$$

FIG. 7.

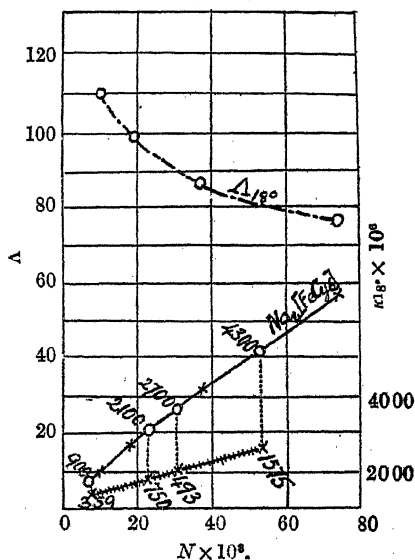
*Sodium ferrocyanide.*

TABLE XIV.

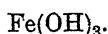
 $\text{Na}_4\text{Fe}(\text{CN})_6$ .

$N \times 10^3$	$\kappa_{18^\circ} \times 10^6$	$\Lambda_{18^\circ}$
74	5664	76.6
37	3205	86.8
18.5	1803	97.5
9.3	1000	110.0

A remarkable feature of Fig. 7 is that the curve for the peptising agent in the solution lies below that of the ferrocyanide in water. Hence it was assumed that the conductivity of the colloid was wholly due to the amount of peptising agent present, and therefore the

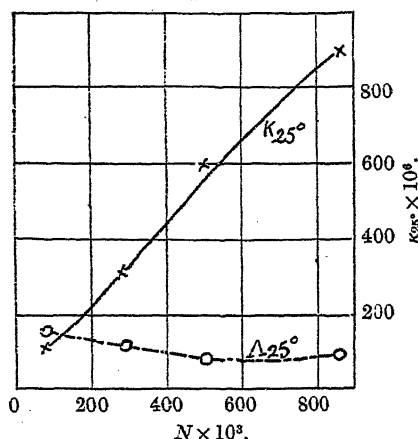
abscissæ of the lowest curve in the figure are those of the peptising agent in Prussian blue solution: the ordinates are corresponding values of equivalent conductivity of Prussian blue. The values are taken from Table XIII. The continuations of these ordinates cut the curve for sodium ferrocyanide in water, and the data at these points of intersection show the conductivities of a pure solution of sodium ferrocyanide of the same concentration as in the colloid. The conductivity curve for sodium ferrocyanide with peptisation

TABLE XV.



Soln.	$N \times 10^3.$	$\kappa_{25^\circ} \times 10^6.$	$\Lambda_{25^\circ}.$
2	71	104.6	1.511
1	144	238.0	1.641
4	293	314.3	1.073
3	513	508.5	1.741
5	967	903.0	0.934

FIG. 8.

*Ferric hydroxide.*

is a straight line, and the gradient of this line with respect to the curve for sodium ferrocyanide in water is about 0.368. Hence the ordinates,  $y_1$ , of the one curve are constant multiples of the ordinates,  $y_2$ , of the other, i.e.,  $y_1 = \text{constant} \times y_2$ . It would be of interest to investigate the behaviour of other colloids in a similar way.

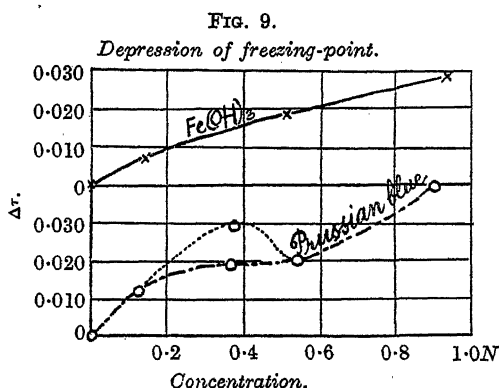
(b) *Ferric hydroxide* (see Table XV and Fig. 8). All the measurements were made at  $25^\circ$ . The curve for equivalent conductivity seems to pass through a minimum at a normality of about 0.5. The equation,  $y_1 = y_2 \times \text{constant}$ , found for Prussian blue, unfortunately, cannot be examined in this case, for the conductivity of



this colloid is far superior to that of the peptising agent—if this alone is considered—as the following data show :

Acetic acid.		Coll. $\text{Fe}(\text{OH})_3$ .		
$N \times 10^3$ .	$\kappa_{25^\circ} \times 10^6$ .	No.	Peptisation ( $N \times 10^3$ ).	$\kappa_{25^\circ} \times 10^6$ .
2	67	2	2	105
5	110	4	3	314
10	158	3	9.6	509
20	229	5	11.0	903

The figures in this table show that ions of acetic acid—and it may be others as well—transport electric charges. These others, especially chlorine ions, may arise from impurities adsorbed by the ferric hydroxide when it was first precipitated and irremovable by washing. The discussion which follows later shows that the



greater conductivity of these solutions of ferric hydroxide may possibly be due to "colloidal ions."

4. *Depression of Freezing-point.*—These determinations, which were carried out in a Beckmann apparatus, were made in order to estimate, as far as possible, the relative numbers of particles in the solutions and also to determine whether these numbers vary proportionally to the concentration. The results are in Table XVI (see also Fig. 9).

TABLE XVI.  
*Freezing-point Depression,  $\Delta t$ .*

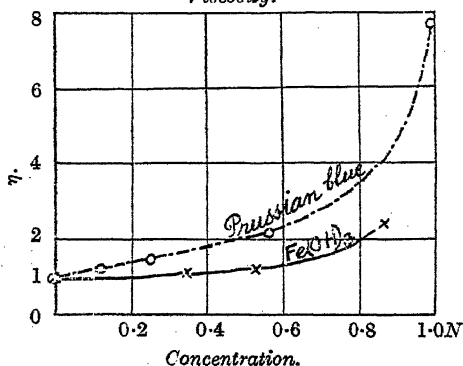
Prussian blue.			Ferric hydroxide.		
Soln.	Conc. ( $N$ ).	$\Delta t$ .	Soln.	Conc. ( $N$ ).	$\Delta t$ .
1	0.896	0.040°	5	0.967	0.029°
2	0.51	0.020	3	0.513	0.018
3	0.37	{ 0.030** 0.019**	1	0.144	0.008
4	0.126	0.012			

A small freezing-point depression is an indication of the comparative purity of a colloidal system. The values marked \*\* in the table were obtained at different times and the value 0.030 was constant. The curve may possibly rise to a maximum for a concentration of 0.3*N*, or there may here be a point of inflexion if the lower and more probable value, 0.019, be plotted.

TABLE XVII.  
*Viscosities at 25°.*

Ferric hydroxide.				Prussian blue.			
Soln.	<i>s.</i>	<i>t</i> (secs.).	$\eta$ .	Soln.	<i>s.</i>	<i>t</i> (secs.).	$\eta$ .
H <sub>2</sub> O	0.9960	62.8	1.000	H <sub>2</sub> O	0.9960	62.8	1.000
2	0.9982	63.7	1.017	4	1.0029	73.0	1.170
I	1.0046	67.8	1.089	II	1.0085	84.4	1.361
II	1.0089	72.0	1.161	I	1.0219	128.8	2.104
III	1.0171	150.6	2.448	III	1.0442	446.7	7.452

FIG. 10.  
*Viscosity.*



The molecular weights of ferric hydroxide calculated from the results are 2240, 2000, and 1090 for solutions 5, 3, and 1, respectively. These values, of course, carry little weight, but they seem to indicate that with increasing concentration the particles in the solution coalesce to form larger aggregates.

5. *Viscosity.*—These measurements were made because there may be an intimate relation between the viscosity of a colloidal solution and its absorptive power. The apparatus, an Ostwald viscosimeter, was in a large thermostat at 25° and, as usual, two series of experiments were made. The viscosities were calculated by means of the equation  $\eta = \eta_w \cdot st / s_w t_w$ , where  $\eta$  and  $\eta_w$  are the relative viscosities of the solution and water, respectively, *s* is the density of the solution and *t* is the time of flow. The results are in Table XVII and are shown graphically in Fig. 10.

*Discussion of Results.*

An examination of the solubility tables reveals the very different behaviour of the two colloidal solutions towards carbon dioxide and acetylene.

The solubility of carbon dioxide in the more concentrated solutions of ferric hydroxide exceeds its solubility in water by as much as 20%. Moreover, it is almost directly proportional to the concentration—a relation found by Findlay also (*loc. cit.*), although his absolute values of  $l$  were considerably smaller than those now recorded.

Carbon dioxide is also more soluble in solutions of Prussian blue than in water, but only moderately so (at the most, 3–4%). A well-defined maximum occurs in the values of  $l$  at all the temperatures used, in every case at a concentration of 0.3-normal.

Towards acetylene, however, both colloidal solutions display an essentially different behaviour, the solubility of the gas being always less than its solubility in water. The diminution is 1% for ferric hydroxide and 7–8% for Prussian blue (compare Findlay's curves, reproduced in Fig. 5, for nitrous oxide in ferric hydroxide at 25°).

For these colloidal systems the relation between the solubility of gases and the temperature is in accord with the ordinary laws governing the solution of gases, *viz.*, the temperature coefficient is negative and its numerical value increases rapidly with diminishing temperature (see Table VIII). This magnitude appears to be a function of concentration (at constant temperature). The following rule, therefore, may be deduced. At a given temperature, the numerical value of the temperature coefficient varies, with increasing concentration, as the absorptive power of the colloidal solution for the dissolving gas. For instance, in the system carbon dioxide–ferric hydroxide,  $l$  increases rapidly with  $c$  and consequently the quotient  $\Delta l/\Delta t$  increases as  $c$  increases: or, in the system acetylene–ferri ferrocyanide,  $l$  diminishes greatly as  $c$  increases, and consequently  $\Delta l/\Delta t$  decreases as  $c$  increases. Such behaviour, however, is not so well defined in the systems carbon dioxide–ferri ferrocyanide and acetylene–ferric hydroxide, since  $l$  varies but little. In the latter case, a diminution even of the temperature coefficient might be assumed owing to the small diminution of  $l$ .

The factors which may account for the observed phenomena are (1) the chemical nature of the colloid and of the gas absorbed (chemical combination), (2) the influence of the specific surface (adsorption), (3) the nature of the electric change, and (4) temperature.

1. *Chemical nature.* This is, presumably, the most important factor in all absorption phenomena, but, unfortunately, it is still

very obscure. Clearly, the more inert the gas and the colloidal solution are chemically, the smaller will be the effect of this factor. An obvious conclusion from this is that  $l$  for the systems carbon dioxide-Prussian blue and acetylene-ferric hydroxide will differ but little from the value of  $l$  for water, since fairly inert substances meet each other. On the other hand, a chemical reaction may be expected to take place between the basic ferric hydroxide and the acidic carbon dioxide. It is true that there is as yet no evidence of the existence of a compound  $\text{Fe}_2(\text{CO}_3)_3$ . Since, however, electro-positive ferric hydroxide, according to Pauli and Mattula (*Kolloid-Z.*, 1917, 21, 49), has the constitution  $[\alpha\text{Fe}(\text{OH})_3]_2\gamma\text{Fe}'''$ , and there is formed by the dissociation of the dissolved carbon dioxide a small amount of  $\text{CO}_3''$ , a combination of this with the trivalent iron to give complex colloidal  $\{[\alpha\text{Fe}(\text{OH})_3]_2\gamma\text{Fe}\}_2(\gamma\text{CO}_3)_3$  may reasonably be assumed. This assumption seems to be justified by the strikingly high conductivity of the colloidal solution, which far exceeds that due to the peptising agent present.

2. *Specific surface.* The present results, as well as those of Geffcken and Findlay, clearly show that some factor is operating in addition to adsorption. The extent of the latter is determined by the degree of dispersion, and to account for the different behaviour of the two colloids by adsorption alone the specific surface of the ferric hydroxide would have to be 8—10 times larger than that of the Prussian blue—an assumption that cannot be justified.

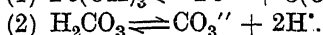
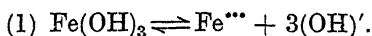
Dispersion, however, has an effect, and to determine it the absorption of carbon dioxide for different dispersions of ferric hydroxide at the same concentration (0.066*N*) was measured.

*Values of  $l$ .*

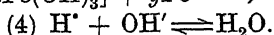
	25°.	20°.	15°.	10°.
High dispersion .....	0.854	0.961	1.095	1.268
Low dispersion .....	0.817	0.930	1.068	1.239
Water .....	0.826	0.936	1.070	1.240

At the higher temperatures the absorptive power of the less highly dispersed system is markedly depressed, even below that of water. This diminution, however, depends not only on the specific surface of the colloid, but also on the quantity of peptising agent present. In the less highly dispersed system this was 0.3% and the basic character of the ferric hydroxide was greatly diminished and its electrical nature correspondingly changed.

3. *Electric change.* The changes that take place when carbon dioxide is in contact with a colloidal solution of ferric hydroxide may be represented by the following scheme; for a given temperature and pressure a definite equilibrium will be set up :



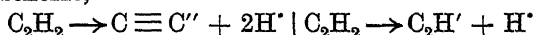
(3) The colloidal particles become associated with  $\text{Fe}^{+++}$ :  
 $[\text{xFe(OH)}_3] + \text{yFe}^{+++} \rightarrow [\text{xFe(OH)}_3]\text{yFe}^{+++}.$



(5)  $2[\text{xFe(OH)}_3]\text{yFe}^{+++} + 3\text{yCO}_3'' \rightleftharpoons \{[\text{xFe(OH)}_3]\text{yFe}\}_2 (\text{yCO}_3)_3.$   
 (compare Pauli and Mattula, *loc. cit.*).

The remarkably high solubility of carbon dioxide in ferric hydroxide and the readiness with which the gas is expelled by heating may thus be explained.

The preceding explanation involves the basic character of ferric hydroxide, the positive charge on the colloidal particles, and the acid nature of the gas. The last factor may for all practical purposes be neglected in the case of acetylene and nitrous oxide. Geffcken (*loc. cit.*, p. 301) has shown the indifferent nature of nitrous oxide by conductivity determinations with saturated aqueous solutions. The following measurements, made by the author, reveal the slight increase in conductivity that occurs when water is saturated with acetylene: water 2.18, 2.81,  $2.94 \times 10^{-6}$ ; mean  $2.63 \times 10^{-6}$ . Water saturated with acetylene 5.64, 4.98,  $4.03 \times 10^{-6}$ ; mean  $4.88 \times 10^{-6}$ . This result is in agreement with the investigations of Billitzer (*Z. physikal. Chem.*, 1902, 40, 535), who pointed out a very slight dissociation of acetylene, represented by the following scheme,



and found that the gas in saturated aqueous solution at atmospheric pressure corresponds to an acid about 400 times weaker than carbonic acid. Acetylene, therefore, and nitrous oxide may be regarded as inert gases, and their similar behaviour towards ferric hydroxide is thus satisfactorily explained. It is chiefly absorption that takes place, and this accounts, to some extent at least, for the diminution of solubility which occurs with increasing concentration. The large decrease of  $l$  for the system acetylene-Prussian blue is attributable to the high concentration of the colloid (above 7%), in comparison with that of the ferric hydroxide (3%), and to its negative charge.

4. *Temperature.* The rule stated on p. 313 may be explained on the basis of the kinetic theory. If the solubility increases with the concentration, the content both of colloid and of gas particles in the solution also increases and the conditions for the presence of gas particles become less favourable; so the rate of diminution of solubility per  $1^\circ$  rise in temperature becomes greater. A decrease in solubility with increasing concentration favours the retention of the gas particles in the solution: hence the diminished quantity

of gas corresponding with  $1^\circ$  may be expected to remain constant or even to fall.

*Summary.*

1. Two typical, highly concentrated colloidal solutions have been prepared, and a very highly dispersed system of ferric hydroxide has been obtained by a modification of P. de St. Gilles's method.

2. Measurements of the solubility of carbon dioxide and acetylene in these systems have been made at five temperatures and different concentrations, and the temperature coefficients determined.

3. The colloids have been characterised by determinations of density, concentration, conductivity, viscosity, and depression of freezing-point.

4. Certain regularities in solubility have been found and an attempt has been made to analyse the factors that produce them.

The author wishes to express his thanks to Dr. Charles Brunner, and to acknowledge his indebtedness to the late Dr. Chas. Hopfgartner, at whose suggestion the work was undertaken.

INNSBRUCK,  
SILLGASSE, 2.

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## *XL.—The Reciprocal Salt Pair (Na, Ba)–(Cl, NO<sub>3</sub>) in Aqueous Solution at 20°.*

By ALEXANDER FINDLAY and JAMES CRUICKSHANK.

THE investigation of this system was undertaken with a view to ascertain the best conditions for the preparation of barium nitrate from the chloride by interaction with sodium nitrate. The most important equilibria were investigated by one of us in 1917, and the further investigation of the system was taken up later with the intention of completing the equilibrium data at  $20^\circ$  and of extending the study also to higher temperatures. This extension of the investigation, however, has been rendered unnecessary by the work of Coppadoro (*Gazzetta*, 1912, 42, 1; 1913, 43, 138). We have restricted ourselves, therefore, to an examination of the equilibria at  $20^\circ$ .

The following values have been determined for the composition of aqueous solutions in equilibrium with one, two, and three salts, respectively, included in the above reciprocal salt pair.

1. Single salts.

Solid phase.	G. of anhydrous salt in 100 g. of soln.	Solid phase.	G. of anhydrous salt in 100 g. of soln.
NaCl	26.40	BaCl <sub>2</sub> .2H <sub>2</sub> O	26.32
NaNO <sub>3</sub>	46.77	Ba(NO <sub>3</sub> ) <sub>2</sub>	8.41

2. System NaCl-BaCl<sub>2</sub>-H<sub>2</sub>O.

Solid phase.	Percentage composition of solutions.		
	NaCl.	BaCl <sub>2</sub> .	H <sub>2</sub> O.
NaCl	25.28	1.65	73.07
NaCl; BaCl <sub>2</sub> ·2H <sub>2</sub> O	24.59	3.07	72.34
BaCl <sub>2</sub> ·2H <sub>2</sub> O	21.23	4.17	74.60
"	18.52	6.51	74.97
"	14.50	10.04	75.46
"	9.54	14.99	75.47
"	7.80	16.89	75.31

3. System NaCl-NaNO<sub>3</sub>-H<sub>2</sub>O.

Solid phase.	Percentage composition of solutions.		
	NaCl.	NaNO <sub>3</sub> .	H <sub>2</sub> O.
NaCl	18.49	18.62	62.89
"	17.34	21.30	61.36
NaCl; NaNO <sub>3</sub>	13.80	30.34	55.86
NaNO <sub>3</sub>	9.56	34.85	55.58
"	7.67	37.18	55.15

4. System BaCl<sub>2</sub>-Ba(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O.

Solid phase.	Percentage composition of solutions.		
	BaCl <sub>2</sub> .	Ba(NO <sub>3</sub> ) <sub>2</sub> .	H <sub>2</sub> O.
BaCl <sub>2</sub> ·2H <sub>2</sub> O	26.07	1.31	72.62
BaCl <sub>2</sub> ·2H <sub>2</sub> O; Ba(NO <sub>3</sub> ) <sub>2</sub>	25.09	6.93	67.98
Ba(NO <sub>3</sub> ) <sub>2</sub>	20.81	6.54	72.65
"	12.31	6.72	80.97
"	7.51	7.17	85.32

5. System NaNO<sub>3</sub>-Ba(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O.

Solid phase.	Percentage composition of solutions.		
	NaNO <sub>3</sub> .	Ba(NO <sub>3</sub> ) <sub>2</sub> .	H <sub>2</sub> O.
NaNO <sub>3</sub> ; Ba(NO <sub>3</sub> ) <sub>2</sub>	45.74	1.86	52.40
Ba(NO <sub>3</sub> ) <sub>2</sub>	37.07	2.07	60.86
"	14.59	2.49	82.92
"	5.61	3.89	90.50

## 6. Quaternary Solutions.

Solid phase.	Percentage composition of solutions.				
	NaCl.	NaNO <sub>3</sub> .	Ba(NO <sub>3</sub> ) <sub>2</sub> .	BaCl <sub>2</sub> .	H <sub>2</sub> O.
NaNO <sub>3</sub> ; Ba(NO <sub>3</sub> ) <sub>2</sub>	6.57	37.82	1.62	—	53.99
NaCl; Ba(NO <sub>3</sub> ) <sub>2</sub>	15.79	24.08	0.14	—	59.99
BaCl <sub>2</sub> ·2H <sub>2</sub> O; Ba(NO <sub>3</sub> ) <sub>2</sub>	2.02	—	6.49	22.66	68.83
NaCl; Ba(NO <sub>3</sub> ) <sub>2</sub> ; NaNO <sub>3</sub>	14.23	29.75	0.13	—	55.89
NaCl; Ba(NO <sub>3</sub> ) <sub>2</sub> ; BaCl <sub>2</sub> ·2H <sub>2</sub> O	24.16	0.50	7.14	—	68.20

The last noted solution is incongruently saturated.

For the practical application of the above determinations, the following numbers are of interest :

Initial composition of mixture (g. of anhydrous salt per 1000 g. of water).		Percentage of salt precipitated as Ba(NO <sub>3</sub> ) <sub>2</sub> .	
NaNO <sub>3</sub> .	BaCl <sub>2</sub> .	BaCl <sub>2</sub> .	NaNO <sub>3</sub> .
283	337.8	76.45	74.45
471.8	337.8	92.55	54.06

It will, in general, be advantageous to use a relatively large proportion of sodium nitrate in the initial mixture so as to obtain as complete a utilisation as possible of barium chloride. The mother-liquor containing sodium nitrate can be used, after evaporation and separation of the sodium chloride, for the conversion of a further quantity of barium chloride.

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[Received, December 31st, 1925.]

## XLI.—*The Equilibrium between Ethyl Alcohol and the Alkali and Alkaline-earth Salts. Part I.*

By DAVID GLYNWYN ROBERT BONNELL and WILLIAM JACOB JONES.

THE first investigator in this field was Graham (*Phil. Mag.*, 1828, 4, 265, 331), who prepared the ethyl alcoholate of calcium chloride. His work was repeated by Einbrodt (*Annalen*, 1848, 65, 115), by Chodnew (*Bull. Acad. St. Petersburg*, 1865, 8, 150), by Heindl (*Monatsh.*, 1881, 2, 200), and by Menshutkin (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 1010). The calcium bromide tri-alcoholate (Roques, *J. Pharm.*, 1895, 1, 301), the hexa-alcoholates of magnesium chloride (Simon, *J. pr. Chem.*, 1879, 20, 371), bromide and iodide (Menschutkin, *Bull. St. Petersburg Polytec. Inst.*, 1906, 3, 12), the tetra-alcoholates of lithium chloride (Simon, *loc. cit.*) and bromide (Turner and Bissett, *J.*, 1914, 105, 1783) have all been described. Solubility determinations over ranges of temperatures have been carried out as follows: lithium chloride (Turner and Bissett, *J.*, 1913, 103, 1904), sodium and potassium iodides (Tyrer, *J.*, 1910, 97, 621) and calcium chloride (Menschutkin, *loc. cit.*).

The purpose of the present series of investigations was to determine the following: (1) The solubility over a wide range of temperature. (2) The composition of the various solid phases. (3) The transition temperatures. In the present paper are described the conditions of equilibrium between ethyl alcohol and the following salts: lithium bromide, sodium bromide, calcium bromide, barium bromide, and barium iodide.

### EXPERIMENTAL.

For obvious reasons great attention was directed to the purity of the substances used, and especially to their freedom from traces of water, since, owing to the far greater affinity of salts for this than for alcohol, the composition of the solid phase is particularly influenced by its presence.

The alcohol was purified by Lapworth's method (*J.*, 1910, 97, 24).



The densities, without correction of the weighings to vacuum, of the two specimens that were used in the present work were  $d_4^{25}$  0.78494 and 0.78496. Great care was exercised both during the purification and preservation and in subsequent work to exclude atmospheric moisture.

The salts were purified by recrystallisation from water and then dehydrated by Turner and Bissett's method (P., 1913, 29, 233) (Found by the gravimetric silver halide method: LiBr 99.81, NaBr 99.93, CaBr<sub>2</sub> 99.90, BaBr<sub>2</sub> 99.89, BaI<sub>2</sub> 99.87%).

The graduated vessels, weights and thermometers had been carefully standardised. In the solubility determinations above 20° ordinary thermostats, which kept constant within 0.02°, were used. At 15° and at 10°, the temperature was maintained constant within 0.04° by a regulated inflow of cold water and by continuous and vigorous stirring. For 0°, a bath of washed, finely powdered ice was used. In each determination the anhydrous salt and alcohol were put together in a clean, dry, glass-stoppered flask, which thereafter was kept in the thermostat, and as far as possible in the dark. A tightly fitting, thick paper cap was tied over the stopper. The mixtures were shaken by hand at intervals over a long period, and a portion of the solution was then withdrawn for analysis after the solid had settled completely. Thereafter the mixtures were again shaken and the procedure described was repeated until two consecutive analyses agreed within the experimental error. By operating in this manner saturation was ensured and incursion of atmospheric moisture was better precluded than if an internal stirring arrangement had been used. In some of the experiments, the equilibrium point was approached by first preparing a saturated solution at a temperature at which the solubility was greater than at the temperature under investigation, then placing it in the thermostat at the latter temperature, and, after keeping it therein for some time with frequent shaking, analysing the liquid phase. In all cases, the solubility so found was identical with that found by the procedure previously described. There can therefore be no doubt that in our experiments the systems were truly in equilibrium when the solubility determinations were made.

For the determination of the composition of the solid phase a small quantity was scooped out, quickly dried between filter-paper, and analysed. For such solid phases as were stable only at temperatures much above the ordinary, the procedure was modified as follows. Some of the salt was suspended by means of a basket of metal gauze in a saturated solution in a stoppered flask, which was immersed in the thermostat. When equilibrium had been attained, the basket was drawn up into the vapour space above the solution

and was there allowed to drain. When draining was complete, the solid in the basket was withdrawn and analysed.

The transition temperatures obtained by the solubility determinations were confirmed by the dilatometric method.

### Results.

Solubility in gram of salt per gram of alcohol, of					
Temp.	sodium bromide.	barium bromide.	barium iodide.	calcium bromide.	lithium bromide.
0°	0.02445	0.05880	0.7775	0.4670	0.3261
10	0.02379	0.05067	0.7735	0.4801	0.3602
15	0.02343	0.04590	—	0.5051	—*
20	0.02322	0.04130	0.7700	0.5350	—*
25	0.02314	—	—	0.5395	0.7210
30	0.02292	0.03322	0.7660	0.5552	0.7251
40	0.02276	0.02433	0.7620	0.6011	0.7303
50	0.02259	0.01837	0.7585	0.6564	0.7752
60	0.02312	0.01479	0.7550	0.7602	0.8284
70	0.02345	0.01253	0.7510	0.9381	0.8913
75	—	—	—	1.0220	0.9412
80	—	—	—	1.0310	0.9910
85	—	—	—	1.0610	—

\* Retroflex region (see later table).

All the above values were determined directly.

Throughout in the cases of sodium bromide, barium bromide, and barium iodide the solid phases were respectively NaBr, BaBr<sub>2</sub>, and BaI<sub>2</sub>.

In the case of calcium bromide, below 17.0° the solid phase is CaBr<sub>2</sub>·4C<sub>2</sub>H<sub>5</sub>·OH, between 17.0° and 73.9° CaBr<sub>2</sub>·3C<sub>2</sub>H<sub>5</sub>·OH, and above 73.9° CaBr<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>·OH (CaBr<sub>2</sub>·4C<sub>2</sub>H<sub>5</sub>·OH: ethyl alcohol found, 48.6; calc., 48.0%. CaBr<sub>2</sub>·3C<sub>2</sub>H<sub>5</sub>·OH: ethyl alcohol found, 42.4; calc., 40.9%. CaBr<sub>2</sub>·C<sub>2</sub>H<sub>5</sub>·OH: ethyl alcohol found, 20.5; calc., 18.7%). The form of the solubility curves exhibits a close parallelism to those of calcium chloride in water and in methyl alcohol.

When lithium bromide and alcohol were brought together, great heat was developed and a solution of a slightly brown tint was obtained. At 25° and 30° the solution was very viscous, and consequently took a long time to settle sufficiently to allow of measurements being taken. In the temperature range 13.2° to 23.8° there is a retroflex region, the solid phase being LiBr·4C<sub>2</sub>H<sub>5</sub>·OH (ethyl alcohol found, 69.2; calc., 67.9%). The congruent melting point of the tetra-alcoholate was 23.8°, and the solid phase in contact with the saturated solution at the higher temperatures has the composition LiBr. The eutectic point for the anhydrous salt and the alcoholate is 13.2°. The alcoholate crystallises in flat plates which are highly deliquescent in the atmosphere, and, owing to the

hygroscopicity of the salt, it was impracticable to determine its affinity for alcohol. Greater detail regarding the eutectic region is given in the following table :

Retroflex Region of the Solubility of Lithium Bromide in Ethyl Alcohol.

Solubility in gram of lithium bromide per gram of ethyl alcohol with solid phases.

Temp.	LiBr.	LiBr, 4C <sub>2</sub> H <sub>5</sub> .OH.	LiBr, 4C <sub>2</sub> H <sub>5</sub> .OH.
13.2°	0.700	0.700	0.700
15.0	0.702	0.687*	0.381
16.0	0.704	0.675*	0.390
20.0	0.708	0.606*	0.420
23.0	0.712	0.530*	0.460
23.8	0.713	0.472	0.472

The asterisked values were obtained by thermal analysis, the remaining values being obtained either by direct determinations of solubility or from a graph.

When the barium iodide was brought into contact with the alcohol great heat was developed, and in a short time the solution acquired an orange tint due to the presence of traces of free iodine. A fresh solution was made in a black flask, but even in this the colour again developed and it was found impossible to obtain colourless solutions.

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[Received, November 28th, 1925.]

## XLII.—The Dissociation Pressures of Alcoholates. Part I.

By DAVID GLYNWYN ROBERT BONNELL and WILLIAM JACOB JONES.

No account of work on this subject has yet been published, and because of its importance in relation to the affinity of salts for the alcohols and to residual affinity in general, we have undertaken the present investigation.

The methods, which are applicable in the case of hydrates, may be divided into the following classes : (a) indirect, (b) tensimetric, and (c) dynamical, or gas current saturation. In the following, the applicability of each method is discussed.

Among indirect methods are those of Müller-Erbach (*Ber.*, 1881, 14, 1093; *Z. physikal. Chem.*, 1888, 2, 113), Wilson (*J. Amer. Chem. Soc.*, 1921, 43, 704), Lescœur (*Ann. Chim. Phys.*, 1889, 16, 378; 1890, 19, 533), Cumming (J., 1909, 95, 1772), Linebarger (*Z. physikal. Chem.*, 1894, 13, 500), Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, 33, 1309), and Noyes and Westbrook (*ibid.*, 1921, 43, 726). Müller-Erbach employed two methods. In the first,

he compared the rates of diffusion of aqueous vapour from water and from the hydrate. His second method was to find the dilution of aqueous sulphuric acid solution over which the hydrate neither gained nor lost weight, and, when this was the case, the dissociation pressure was equal to the known aqueous pressure of the acid solution at the temperature of the experiment. Wilson's method is identical in principle with the latter method of Müller-Erbach. This method might be made applicable to alcoholates if, first, the aqueous sulphuric acid were replaced by an alcoholic solution of a difficultly volatile substance and, secondly, the alcoholic vapour pressures of solutions of various concentrations of this substance in alcohol had been previously determined at various temperatures. The time required for such an investigation might, however, be prohibitive. Both Lescoeur and Cumming determined the dew point of the vapour phase in equilibrium with the pair of hydrates. Their method is directly applicable to the alcoholates, but, where the dissociation pressure is low, suffers from the disadvantage that the steep gradient of temperature in the apparatus introduces a serious source of error. Linebarger found the aqueous vapour pressure of a pair of salt hydrates, at the boiling point of ether, by determining the boiling point of the moist ether in contact and equilibrium with them, and then referring to a table giving the boiling points of various aqueous ether mixtures and their partial aqueous vapour pressures at those temperatures. Foote and Scholes shook a mixture of two hydrates with alcohol, and, after the attainment of equilibrium, determined the water content of the alcoholic layer. The dissociation pressure of the hydrate at the temperature of the experiment is equal to the known partial pressure of a water-alcohol mixture of the same composition as this layer. Noyes and Westbrook have employed a method which in principle is identical with that of Foote and Scholes, the reference liquid used being *iso*-amyl alcohol. In the latter three methods, the properties of the reference liquids are so strictly circumscribed that it would be difficult to find a suitable liquid for use in the investigation of the alcoholates. Thus the salt must be insoluble in the reference liquid, the reference liquid must not form stable solid solvates with the salts in the presence of the alcohols, its affinity for the alcohols must be negligible compared with that of the salts for alcohol, and it must be only partly miscible with alcohol.

In order to apply the tensimetric method of Frowein (*Z. physikal. Chem.*, 1887, 1, 1, 362), a liquid in which the alcohols are insoluble has to be employed in the manometer, and mercury, which is the only practicable liquid, is so dense that accuracy cannot be conveniently obtained by its use. Moreover Menzies (*J. Amer. Chem. Soc.*, 1920,

42, 1952) has found that it is extremely difficult to evacuate the tensimeter satisfactorily.

The dynamical method, which is originally due to Tammann (*Ann. Physik*, 1888, **33**, 329), has been elaborated and perfected for the hydrates by Partington (J., 1911, **99**, 466), Baxter and Lansing (*J. Amer. Chem. Soc.*, 1920, **42**, 419), Partington and Huntingford (J., 1923, **123**, 160), Schumb (*J. Amer. Chem. Soc.*, 1923, **45**, 342), and Baxter and Cooper (*ibid.*, 1924, **46**, 923). We have found that this method is eminently suited to the investigation of the dissociation pressures of the alcoholates.

Two objections have been urged against this method, namely, first, that equilibrium is approached only from the side of undersaturation of the air current, and, secondly, that attainment of equilibrium between vapour phase and crystals is so slow that the time allowed in the passage of the air over the solid is insufficient. The first objection is disposed of by the data in Table I, where some experiments are detailed in which the equilibrium was approached both from undersaturation and from supersaturation, with results which within experimental error are identical. The second objection can be met only by ensuring that the rate of passage of air employed in the experiments is sufficiently slow, and by demonstrating that the same value is obtained for the dissociation pressures when a considerably slower rate is employed. The necessary slowness of the current depends, among other things, on the nature of the solvent, the salt, the temperature, and the dimensions of the saturator used. In our experiments the passage of 100 c.c. per hour gave the same result as that obtained with 500 c.c. per hour, and these were the extreme rates used. Furthermore, the fact that in our experiments air which was initially supersaturated with alcohol vapour gave the same result as air which was initially dry proves that the air leaving the saturator was adequately saturated with alcohol vapour and that a true state of equilibrium was attained.

#### EXPERIMENTAL.

The method adopted in the present work consisted in drawing a measured volume of dry air, free from carbon dioxide, through an intimate mixture of the pair of alcoholates, and finding the weight of alcohol vapour taken up by the air, either by collecting the alcohol in weighed U-tubes containing phosphorus pentoxide, or by determining the loss of weight of the mixture. The air, which was drawn through the mixture of alcoholates by means of an aspirator, was purified by passage in succession through concentrated sulphuric acid, a large calcium chloride tower, a U-tube filled with broken sticks of potassium hydroxide, and finally a 210 cm. train of freshly

prepared phosphorus pentoxide powder mixed with glass wool. The purified air passed into the saturator, which was similar in form to that used by Partington (J., 1911, 99, 468, Fig. 1A), except that our U-tubes were sealed off instead of being closed with paraffined corks. The saturator was filled to the level of the side tube with a mixture of the pair of alcoholates under investigation. The diameter of the column of mixture was 2 cm. and its mean length 42 cm. The saturator was immersed in a thermostat with only the side tubes emergent. A differential mercury manometer attached to the exit side tube served to give the difference in pressure between the external atmosphere and the mixture of air and alcohol vapour as it left the saturator, and consequently the sum of the partial pressures of the alcohol and air could be found. The saturated air afterwards passed into a U-tube filled with phosphorus pentoxide mixed with glass wool, whereby it was deprived of its alcohol. All connexions in this part of the apparatus were made with tightly fitting rubber tubing, inside which the ends of the glass tubes were brought into contact with each other. The air next passed into a U-tube filled with calcium chloride, which served as a trap to prevent back-diffusion of moisture from the aspirator in which the air was finally collected. At the beginning of the experiment the aspirator was filled to the top with water, which had been allowed to come to room temperature before the air current was started. The air inlet tube reached practically to the bottom of the water in the aspirator, and the air acquired the temperature of the aspirator during its passage downwards through the inlet tube and upwards through the water to the top of the aspirator, where it collected. The volume of air passed over the alcoholates was found by weighing the water expelled from the aspirator. The temperature of the room was maintained constant. An open-limb differential mercury manometer served to give the difference in pressure between the air collected inside the aspirator and the external atmosphere.

Care was taken that the dry air always entered the saturator at the same end in order that the air leaving the saturator should always come into contact with a mixture of both solid phases. Similar care was taken with the phosphorus pentoxide tube in order to retain all traces of alcohol. Atmospheric moisture was rigorously excluded in the preparation of the alcoholates, and in their transfer to the saturator, which had been previously thoroughly dried by a current of hot air.

The alcoholic dissociation pressure,  $p$ , of the pair of alcoholates under investigation at the temperature of the thermostat is given in mm. of mercury by the equation  $p/p' = v/(V + v)$ , where  $v$  and  $V$  are the respective volumes of alcohol vapour and dry air in the

mixture leaving the saturator at the temperature of the experiment and under the pressure  $p'$ , which is the sum of the partial pressures of the alcohol vapour and air as they leave the saturator, expressed in mm. of mercury. Since we are dealing with a ratio of volumes, the ratio of the pressures is unaltered if we substitute the values of the volumes at  $N.T.P.$ , which can be determined as follows :

$$v = \frac{22410m}{M}; \quad V = \frac{273.1(P-f)W}{(273.1+t)760d},$$

wherein  $m$  is the mass of alcohol in grams lost from the saturator and  $M$  is the molecular weight of the alcohol,  $P$  is the final pressure of the air inside the aspirator,  $f$  is the aqueous vapour pressure at the temperature,  $t^\circ$ , of the aspirator, both pressures being expressed in mm. of mercury,  $W$  is the mass in grams in a vacuum of the water expelled from the latter, and  $d$  its density.

$$\text{Thus } p = \frac{22410 \times 760(273.1+t)p'md}{273.1 \times WM(P-f) + 22410 \times 760(273.1+t)md}.$$

$P$  is determined by taking the barometer reading at the end of the experiment and subtracting therefrom the reading of the aspirator manometer.

The sum of the partial pressures,  $p'$ , is equal to the average barometric pressure during the run minus the average value of the readings of the mercury manometer attached to the exit tube of the saturator.

The mass,  $m$ , of the alcohol lost by the saturator was found either by the increase in weight of the phosphorus pentoxide tube or by the decrease in weight of the saturator, or by both means. In these weighings suitable counterpoises were employed. Both methods agreed, as is shown in the tables.

In a typical experiment the results obtained were as follows :  $\text{CaBr}_2, 3n\text{-C}_3\text{H}_7\cdot\text{OH} - \text{CaBr}_2$  at  $60^\circ$ .  $P$  766.7;  $p'$  764.7;  $t$   $17.7^\circ$ ;  $f$  15.0;  $d$  0.99868;  $W$  4281;  $M$  60.06;  $m$  by loss in weight of saturator 0.2200;  $m$  by gain in weight of phosphorus pentoxide tube 0.2193; giving  $p$  by loss in weight of saturator 15.447, and by gain in weight of phosphorus pentoxide tube 15.398, in both cases in mm. of mercury.

The losses in weight of the saturators recorded in the present experiments were between 0.0148 and 0.6271 g., whilst the volumes of air employed fell between 356.4 and 14155 c.c.

In order to eliminate initial disturbances due to liquid alcohol adhering to the crystalline alcoholates each new charge in the saturator was aged by drawing through it a small volume of dry air before the readings were begun.

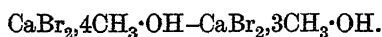
The present method is applicable only where the dissociation

pressure is lower than the vapour pressure of the pure alcohol at room temperature, since, if the former is greater than the latter, condensation will occur in the side tubes which emerge from the thermostat.

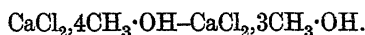
### Results.

In Table I,  $p_i^s$  denotes the values of  $p$  at  $t^s$  determined from super-saturation, and  $p_u^s$  those determined from undersaturation, by the gain in weight of the  $P_2O_5$  tube, and  $p_i^v$  and  $p_g^v$  denote the values of  $p$  determined from the loss in weight of the saturator and the gain in weight of the  $P_2O_5$  tube, respectively.

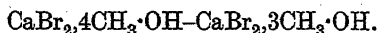
TABLE I.



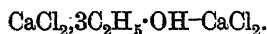
$p_i^{30^s}$	19.99, 19.57, 19.78, 19.82, 19.88.
$p_u^{30^s}$	19.90, 19.90, 19.98, 19.94, 19.92.
$p_i^{30^v}$	40.70, 40.46, 40.58, 40.54, 40.60.
$p_g^{30^v}$	40.42, 40.28, 40.30, 40.28, 40.30.



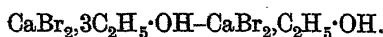
$p_i^{15^s}$	49.90, 49.70, 49.40, 49.60, 50.10, 49.84; mean 49.76.
$p_u^{15^s}$	48.90, 48.99, 48.92, 49.20, 49.09, 48.84; mean 48.84.
$p_i^{20^s}$	70.08, 70.14, 70.06, 70.15, 69.89, 70.00; mean 70.05.
$p_g^{20^v}$	69.80, 69.72, 69.69, 69.73, 69.73, 69.53; mean 69.70.
$p_i^{30^v}$	99.7, 100.5, 99.6, 99.2, 99.5, 99.8; mean 99.7.
$p_g^{30^v}$	98.8, 99.1, 98.6, 98.9, 99.0, 98.9; mean 98.9.



$p_i^{15^s}$	13.55, 13.54, 13.62, 13.58, 13.72; mean 13.60.
$p_u^{15^s}$	13.52, 13.58, 13.59, 13.52, 13.60; mean 13.56.
$p_i^{20^s}$	19.91, 19.92, 19.96, 20.00, 19.93, 20.06; mean 19.96.
$p_g^{20^v}$	19.90, 19.90, 19.98, 19.94, 19.92, 20.02; mean 19.94.
$p_i^{30^v}$	40.45, 40.47, 40.30, 40.43, 40.28, 40.41, 40.36; mean 40.45.
$p_g^{30^v}$	40.42, 40.28, 40.30, 40.28, 40.30, 40.34; mean 40.32.
$p_i^{40^v}$	75.77, 75.80, 74.95, 75.87, 75.85, 75.54, 75.90; mean 75.67.
$p_g^{40^v}$	75.85, 75.50, 75.19, 75.58, 75.01, 75.49, 74.98; mean 75.37.



$p_i^{30^s}$	7.81, 7.53, 8.00, 7.57, 7.72, 7.78; mean 7.74.
$p_i^{40^s}$	17.57, 17.67, 17.57, 17.83, 18.12, 18.28, 17.67, 17.79; mean 17.81.
$p_i^{50^s}$	48.56, 48.89, 48.58, 48.55, 49.40, 49.66, 49.20, 49.01; mean 48.98.



$p_i^{20^s}$	3.89, 3.70, 3.74, 3.92, 3.72, 3.83, 3.73, 3.77; mean 3.79.
$p_i^{30^s}$	9.45, 8.82, 9.06, 9.31, 9.49, 9.40, 9.25, 9.29; mean 9.32.
$p_i^{40^s}$	20.68, 20.18, 20.71, 20.76, 20.40, 20.76, 20.25, 20.95; mean 20.59.
$p_i^{50^s}$	41.48, 41.31, 41.65, 40.20, 41.81, 42.10, 42.00, 41.90; mean 41.55.
$p_i^{60^s}$	73.83, 72.88, 74.50, 73.04, 72.70, 73.40, 72.56, 73.02; mean 73.24.



TABLE I (continued).

 $\text{CaCl}_2, 3n\text{-C}_3\text{H}_7\cdot\text{OH}-\text{CaCl}_2$ .

$p_i^{30^\circ}$	6.41, 6.50, 6.40, 6.44, 6.43, 6.46, 6.45, 6.42, 6.45; mean 6.43.
$p_g^{30^\circ}$	6.40, 6.47, 6.40, 6.39, 6.38, 6.39, 6.42, 6.38, 6.40, 6.40; mean 6.40.
$p_i^{40^\circ}$	16.45, 16.32, 16.16, 16.38, 16.38, 16.28, 16.40, 16.37, 16.38, 16.43; mean 16.36.
$p_g^{40^\circ}$	16.27, 16.18, 16.14, 16.26, 16.31, 16.23, 16.32, 16.28, 16.20, 16.31; mean 16.25.
$p_i^{50^\circ}$	34.10, 34.12, 34.43, 34.30, 34.23, 34.11, 34.24, 34.14, 34.10, 34.37; mean 34.21.
$p_g^{50^\circ}$	34.02, 33.90, 34.34, 34.10, 34.01, 34.00, 34.08, 34.03, 34.03, 34.22; mean 34.17.

 $\text{CaBr}_2, 3n\text{-C}_3\text{H}_7\cdot\text{OH}-\text{CaBr}_2$ .

$p_i^{30^\circ}$	1.70, 1.72, 1.73, 1.67, 1.71, 1.78, 1.70, 1.72, 1.72; mean 1.72.
$p_g^{30^\circ}$	1.70, 1.70, 1.67, 1.67, 1.67, 1.73, 1.69, 1.68, 1.71; mean 1.69.
$p_i^{40^\circ}$	3.73, 3.72, 3.77, 3.77, 3.76, 3.73, 3.76, 3.73, 3.72, 3.74; mean 3.74.
$p_g^{40^\circ}$	3.69, 3.66, 3.70, 3.67, 3.71, 3.66, 3.70, 3.66, 3.71, 3.68; mean 3.68.
$p_i^{50^\circ}$	7.61, 7.67, 7.65, 7.64, 7.66, 7.66, 7.69, 7.68, 7.67, 7.64; mean 7.66.
$p_g^{50^\circ}$	7.47, 7.55, 7.53, 7.55, 7.59, 7.57, 7.62, 7.58, 7.59, 7.55; mean 7.57.
$p_i^{60^\circ}$	15.59, 15.44, 15.63, 15.68, 15.54, 15.45, 15.63, 15.56, 15.50, 15.53; mean 15.56.
$p_g^{60^\circ}$	15.43, 15.18, 15.44, 15.50, 15.50, 15.40, 15.48, 15.42, 15.43, 15.48; mean 15.43.

 $\text{CaCl}_2, 3n\text{-C}_4\text{H}_9\cdot\text{OH}-\text{CaCl}_2$ .

$p_i^{30^\circ}$	1.44, 1.42, 1.48, 1.49, 1.48, 1.46, 1.49, 1.47, 1.47, 1.47; mean 1.47.
$p_g^{30^\circ}$	1.44, 1.43, 1.47, 1.44, 1.43, 1.44, 1.47, 1.43, 1.43, 1.44; mean 1.44.
$p_i^{40^\circ}$	3.96, 3.64, 3.72, 3.66, 3.68, 3.70, 3.72, 3.75, 3.70, 3.70; mean 3.72.
$p_g^{40^\circ}$	3.94, 3.61, 3.68, 3.63, 3.64, 3.68, 3.69, 3.71, 3.70, 3.64; mean 3.69.
$p_i^{50^\circ}$	9.22, 9.18, 9.11, 9.10, 9.20, 9.16, 9.23, 9.15, 9.21, 9.21; mean 9.18.
$p_g^{50^\circ}$	9.08, 9.09, 9.10, 9.06, 9.13, 9.08, 9.21, 9.03, 9.08, 9.18; mean 9.09.
$p_i^{60^\circ}$	13.43, 13.52, 13.82, 13.50, 13.48, 13.55, 13.50, 13.49, 13.56, 13.42; mean 13.53.
$p_g^{60^\circ}$	13.26, 13.32, 13.61, 13.41, 13.39, 13.52, 13.31, 13.27, 13.40, 13.33; mean 13.38.

 $\text{CaBr}_2, 3n\text{-C}_4\text{H}_9\cdot\text{OH}-\text{CaBr}_2$ .

$p_i^{30^\circ}$	1.56, 1.54, 1.59, 1.53, 1.59, 1.54, 1.60, 1.54, 1.56, 1.53; mean 1.56.
$p_g^{30^\circ}$	1.55, 1.52, 1.58, 1.53, 1.55, 1.53, 1.57, 1.54, 1.53, 1.52; mean 1.53.
$p_i^{40^\circ}$	2.84, 2.80, 2.81, 2.78, 2.85, 2.80, 2.81, 2.85, 2.83, 2.82; mean 2.82.
$p_g^{40^\circ}$	2.81, 2.81, 2.79, 2.77, 2.84, 2.79, 2.81, 2.84, 2.82, 2.80; mean 2.81.
$p_i^{50^\circ}$	5.08, 5.04, 5.07, 5.09, 5.05, 5.00, 5.08, 5.08, 4.99, 5.10; mean 5.06.
$p_g^{50^\circ}$	5.06, 5.01, 5.06, 5.08, 5.03, 5.00, 5.04, 5.04, 4.98, 5.05; mean 5.04.
$p_i^{60^\circ}$	9.38, 9.58, 9.36, 9.42, 9.48, 9.54, 9.57, 9.41, 9.45, 9.40; mean 9.46.
$p_g^{60^\circ}$	9.38, 9.48, 9.34, 9.36, 9.43, 9.49, 9.55, 9.41, 9.40, 9.35; mean 9.42.

Table II summarises the preceding results and gives the dissociation pressures in mm. of mercury at the various temperatures.

TABLE II.

Temp.	CaCl <sub>2</sub> 4-3 CH <sub>3</sub> ·OH.	CaBr <sub>2</sub> 4-3 CH <sub>3</sub> ·OH.	CaCl <sub>2</sub> 3-0 C <sub>2</sub> H <sub>5</sub> ·OH.	CaBr <sub>2</sub> 3-1 C <sub>2</sub> H <sub>5</sub> ·OH.	CaCl <sub>2</sub> 3-0 n-C <sub>3</sub> H <sub>7</sub> ·OH.	CaBr <sub>2</sub> 3-0 n-C <sub>3</sub> H <sub>7</sub> ·OH.	CaCl <sub>2</sub> 3-0 n-C <sub>4</sub> H <sub>9</sub> ·OH.	CaBr <sub>2</sub> 3-0 n-C <sub>4</sub> H <sub>9</sub> ·OH.
15°	49·30	13·58	—	—	—	—	—	—
20	69·88	19·95	—	3·79	—	—	—	—
30	99·3	40·39	7·74	9·32	6·42	1·71	1·45	1·55
40	—	75·52	17·81	20·59	16·31	3·71	3·70	2·82
50	—	—	48·98	41·55	34·19	7·62	9·14	5·05
60	—	—	—	73·24	—	15·50	13·45	9·44

Determinations of the dissociation pressures of other alcoholates are now in progress, and it is hoped to make the results obtained and the comparison of the affinities of the alcohols for salts the subjects of a further communication.

We desire to thank the Chemical Society for a grant which partly defrayed the expenses incurred in this investigation.

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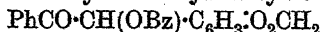
[Received, November 28th, 1925.]

### XLIII.—The 4- and 4'-Methoxybenzoylbenzoins.

By HERBERT GREENE.

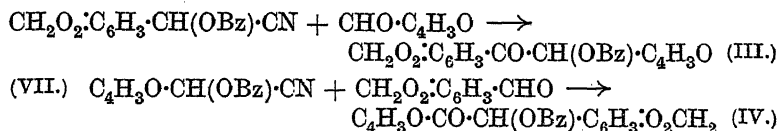
ALKALINE reagents and notably sodium ethoxide convert benzoyl-mandelonitrile (Francis and Davis, J., 1909, 95, 1404) into benzoylbenzoin (Robinson and Robinson, P., 1913, 29, 266; J., 1914, 105, 1456). By adding benzaldehyde to the reaction mixture, Greene and Robinson (J., 1922, 121, 2182) increased the yield of this product and found similarly that benzoylpiperoin was advantageously prepared from a mixture of benzoyl-3:4-methylenedioxy-mandelonitrile and piperonal. These observations were in harmony with Lapworth's view of the course of the benzoin reaction (J., 1903, 83, 1004) and further evidence of a condensation of the aldol type was obtained when the interaction of benzoyl-mandelonitrile and anisaldehyde resulted in the isolation of a methoxybenzoylbenzoin melting at 119·5—120·5°. The structure of this product is discussed below.

It was also shown that 3:4-methylenedioxybenzoylbenzoin,  $\text{CH}_2\text{O}_2\text{:C}_6\text{H}_3\text{CO·CH(OBz)Ph}$  (I), is the main product of condensation between benzoyl-3:4-methylenedioxy-mandelonitrile and benzaldehyde, whereas 3':4'-methylenedioxybenzoylbenzoin,



(II), is obtained from benzoyl-mandelonitrile and piperonal. A migration of the benzoyl group was therefore definitely established. By reducing the time of reaction, these products may be obtained almost pure, and the same is true of the piperonyl-furyl isomerides,

to which, by analogy, structures (III) and (IV) are assigned. The similarity existing between benzaldehyde and furfuraldehyde extends in this case to the yields of "mixed" benzoin. Thus substances (I) and (III) are obtained in small yield only (5 to 10%), whereas piperonal reacts with the benzoylcyanohydrins of these two aldehydes to give substances (II) and (IV) in much larger amount (25 to 30%).



In the same way, anisaldehyde and benzoylmandelonitrile react to give 4'-methoxybenzoylbenzoin (V; m. p. 127—128°), whilst benzoyl-*p*-methoxymandelonitrile and benzaldehyde yield the isomeric 4-methoxybenzoylbenzoin (VI; m. p. 119.5—120.5°). Here, however, the allocation of formulæ is not so simple, for the lower-melting isomeride is also obtainable from the other reaction mixture (Greene and Robinson,\* *loc. cit.*, p. 2189). In fact, either of the isomerides may be obtained from benzoylmandelonitrile and anisaldehyde. The reaction system is very sensitive to changes in the experimental conditions, which have therefore been studied in detail.

On standing in contact with cold sodium ethoxide solution, both isomerides are hydrolysed to *p*-methoxybenzoin (Ekecrantz and Ahlqvist, *Arkiv Kem. Min. Geol.*, 1908, 3, No. 13, 26). It is desirable, therefore, to interrupt the reactions some 15 minutes after addition of the condensing agent, and when this is done the yields are roughly as follows:

	Benzoylmandelonitrile and anisaldehyde.	Benzoyl- <i>p</i> -methoxymandelonitrile and benzaldehyde.
$\frac{1}{2}$ Mol. of NaOEt. Rapid interruption.	Higher-melting isomeride, 30%.	No crystalline product.
1 Mol. of NaOEt. Rapid interruption.	Lower-melting isomeride, 8%.	Lower-melting isomeride, 15%.
$\frac{1}{2}$ Mol. of NaOEt. Gradual addition.	Both isomerides.	Benzoylbenzoin.

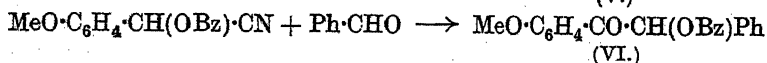
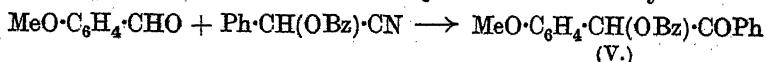
In the cases mentioned above, the diminution of the quantity of sodium ethoxide to a half-molecular proportion leads to the spontaneous separation of substances I, II, III, and IV. It seems reasonable, therefore, to regard the isomeride melting at 127—128° as the normal product of condensation between benzoylmandelonitrile and anisaldehyde, and this substance is therefore 4'-methoxybenzoylbenzoin. The isomeride of m. p. 119.5—120.5° is accord-

\* Compare this communication for the scheme of numbering.

ingly 4-methoxybenzoylbenzoin and its occurrence as a product of condensation of benzoylmandelonitrile and anisaldehyde appears to be due to a double decomposition which results in the formation of benzaldehyde and benzoyl-*p*-methoxymandelonitrile. The following results demonstrate that such a reaction can occur. Attempted condensations of benzoylmandelonitrile and furfuraldehyde on the one hand and of benzoylfurfuraldehydecyanohydrin (VII) and benzaldehyde on the other have uniformly furnished mixtures of benzoylbenzoin (m. p. 125°) and benzoylfuroin (m. p. 92—93°) in slightly varying proportions.

It is clear that the formation of benzoylfuroin from benzoylmandelonitrile and furfuraldehyde involves preliminary transference of the benzoyl cyanide addenda from benzaldehyde to furfuraldehyde. The benzoylfurfuraldehydecyanohydrin so formed then reacts with unchanged furfuraldehyde in the normal manner, and benzoylfuroin is, in fact, readily accessible through this derivative. In the second series of experiments, we have the inverse change. Some benzoylmandelonitrile is formed at the expense of the benzoylfurfuraldehydecyanohydrin, and it then reacts with unchanged benzaldehyde, yielding benzoylbenzoin. All these reaction mixtures originally contained excess of free aldehyde, and accordingly, where the gradual addition of sodium ethoxide during a period of three or four hours has favoured equilibrium, the products of this type of change are present in relatively greater amount.

Under similar conditions, benzoylbenzoin was actually the only crystalline product obtained from benzoyl-*p*-methoxymandelonitrile and benzaldehyde (table above). Here again we must infer degradation of the original nitrile and formation of benzoylmandelonitrile, which subsequently undergoes its normal condensation with unchanged benzaldehyde. With benzoylmandelonitrile and anisaldehyde, the concomitant processes are represented by the scheme below, in which it has not been considered necessary to illustrate the contemporaneous formation of benzoylbenzoin and benzoylanisoin.



In the studies now recorded, the formation of isomeric derivatives of mixed benzoins was observed in three out of four cases. It is apparently favoured by disparity of the constituent aldehydes.

#### EXPERIMENTAL.

*Benzoylfurfuraldehydecyanohydrin.*—Always a good and, on one occasion, a practically theoretical yield of this substance was

obtained by application of the general method of Francis and Davis (*loc. cit.*). Furfuraldehyde (24 g.), benzoyl chloride (35 g.), and a solution of potassium cyanide (17 g.) in water (200 c.c.) were shaken together for 1 hour with cooling. The product separated from 90% alcohol in colourless, hexagonal plates (Found: C, 68.9; H, 4.3.  $C_{13}H_9O_3N$  requires C, 68.7; H, 4.0%). This material, m. p. 48°, was used for the preparation of the derivatives described below. Distillation under reduced pressure and recrystallisation from alcohol raise the melting point to 49°.

*Benzoylfuroin*,  $C_4H_3O \cdot CO \cdot CH(OBz) \cdot C_4H_3O$ .—A cold solution of sodium ethoxide (0.6 g. of sodium) in ethyl alcohol (30 c.c.) was rapidly added to one of benzoylfurfuraldehydecyanohydrin (11 g.) and furfuraldehyde (12 g.) in ethyl alcohol (25 c.c.). The reaction mixture was shaken for 4 minutes in running water, which checked a slight rise of temperature, and then cooled in ice-water. The product that separated was collected after 15 minutes and extracted with boiling ethyl alcohol (20 c.c.). The filtered solution yielded 6.15 g., m. p. 92–93° (Found for twice recrystallised material: C, 68.7; H, 4.1.  $C_{17}H_{12}O_5$  requires C, 68.9; H, 4.0%); a further 1.2 g., m. p. 91–93°, could be isolated. The substance separates from alcohol in colourless octahedra, the predominant prismatic modification being derived by prolongation along one axis. With cold concentrated sulphuric acid, an intense green colour is developed and this gradually changes to brown on warming. By the action of alcoholic sodium ethoxide, a small amount of furil, m. p. 164°, was produced, which was identified by the melting point of its mixture with an authentic sample (E. Fischer, *Annalen*, 1882, 211, 221).

*Benzfuroin*.—It seemed possible to clear up the question as to whether benzfuroin (E. Fischer, *loc. cit.*) is a single substance by benzoylating it and comparing the product with the isomeric benzoylbenzfuroins.

Benzfuroin was recovered unchanged after being shaken with aqueous potassium hydroxide and benzoyl chloride, even in presence of ether, or with pyridine and benzoyl chloride, and heating with the acid chloride alone resulted in profound decomposition. Difficulties of quite another kind were met in attempts, described in detail below, to prepare the isomeric derivatives; for the most part, mixtures of benzoylbenzoin and benzoylfuroin were obtained. Neither of the required isomerides being present in isolable amount, this method of attack was abandoned. There are, however, grounds for believing that benzfuroin is a mixture of two isomerides.

The melting points of four preparations of benzfuroin showed variations (recorded: 135–141°, 134–135°, 134–137°, 138–140°).

These may, of course, be due in part to the presence of benzoin or furoin. Benzofuroin was the sole product isolated in an attempt to prepare a benzoylbenzfuroin by the very slow addition, during 5 or 6 hours with water cooling, of sodium ethoxide (1.15 g. of sodium) in ethyl alcohol (40 c.c.) to a cold solution of benzoylmandelonitrile (11 g.) and furfuraldehyde (12 g.) in ethyl alcohol (40 c.c.). The product (1.9 g.) was isolated by means of ether and crystallised from boiling water, giving 0.5 g. of long, feathery crystals, m. p. 139—141°. The granular, amorphous residue was recrystallised from a little absolute alcohol and then from aqueous alcohol. This material (0.2 g.) melted at 141.5—143.5°, and at 138—140° when mixed with the other fraction or with benzofuroin (m. p. 137—139°) prepared by Fischer's method. The possibility that benzofuroin was here the product of hydrolysis again suggests its composite character. Finally, apart from decomposition, the material was practically unchanged by the action of boiling alcoholic sodium ethoxide, a reagent which doubtless induces enolisation. The recovered material softened at 136° and melted at 140—142°, alone or mixed with the original material.

*Attempts to prepare Isomeric Benzoylbenzfuroins.*—In each experiment the reaction mixture was treated with ether and water. The ethereal layer was washed successively with aqueous sodium bisulphite, sodium carbonate solution, and water, and dried with anhydrous sodium sulphate. The following table summarises the results of the experiments.

		Products from	
		Benzoylmandelonitrile and furfuraldehyde.	Benzoylfurfuralde- hydecyanohydrin and benzaldehyde.
½ Mol. of NaOEt.	Rapid interruption.	Benzoylbenzoin and benzoylfuroin.	Benzoylbenzoin and benzoylfuroin.
1 Mol. of NaOEt.	Rapid interruption.	Ditto (together with benzofuroin).	Benzoylbenzoin and benzoylfuroin (A).
½ Mol. of NaOEt.	Gradual addition.	Ditto (richer in benzoylfuroin).	Ditto (richer in benzoylbenzoin).

The following is a typical experiment resulting in the formation of the product (A). A solution of sodium ethoxide (1.15 g. of sodium) in ethyl alcohol (30 c.c.) was added in one portion to one of benzoylfurfuraldehydecyanohydrin (11.4 g.) and benzaldehyde (10 g.) in ethyl alcohol (30 c.c.). The mixture was shaken in running water for 15 minutes and then extracted as above. After removal of solvent and addition of a little methyl alcohol, crystals readily separated, which were filtered off after 3 hours (4.3 g.). Recrystallised from 90% alcohol (15 c.c.), they melted at 87—88° and showed under the microscope a variety of shapes strongly resembling those observed in the case of 4-methoxybenzoylbenzoin. This crop was

recrystallised from 90% alcohol (15 c.c.), giving two crops, and a third by addition of water: Crop I, 2.45 g., m. p. 86—87°; crop II, 0.75 g., m. p. 87°; crop III, 0.26 g., m. p. 85—87°. Crop I, recrystallised from absolute alcohol, gave two crops, of which the larger weighed 2.19 g. and melted at 86—87°. It still showed a variety of shapes under the microscope (Found: C, 74.0; H, 4.7.  $C_{21}H_{16}O_3 + C_{17}H_{12}O_5$  requires C, 74.5; H, 4.6%). For comparative purposes, an equimolecular mixture of benzoylfuroin and benzoylbenzoin was prepared. After preliminary softening, this began to melt at 85.5° and still contained some solid at 90°, whilst when mixed with product (A) it melted at 84.5—88°. This leads us to conclude that both mixtures are in the neighbourhood of the eutectic. Product (A) is therefore a mixture containing benzoylfuroin, benzoylbenzoin, and probably some benzoylbenzfuroin, although this has on no occasion been isolated.

4-Methoxybenzoylbenzoin (VI; m. p. 119.5—120.5°).—This substance, obtained with fortuitous ease from a reaction mixture of benzoylmandelonitrile and anisaldehyde, was described (Greene and Robinson, *loc. cit.*) as 4'-methoxybenzoylbenzoin. Reasons for adopting the alternative configuration have now been given.

4-Methoxybenzoylbenzoin is best prepared by condensing benzoyl-*p*-methoxymandelonitrile and benzaldehyde. The reaction requires rather more than 1 mol. of sodium ethoxide and should be rapidly interrupted. Thus 1.5 g. of nearly pure material were obtained when a solution of sodium ethoxide (0.6 g. of sodium) in alcohol (20 c.c.) was added in one portion to the nitrile (7.3 g.) and benzaldehyde (10 g.) in cold alcoholic solution (20 c.c.). The reaction lasted 10 minutes.

To observe the abnormal production of this isomeride from benzoylmandelonitrile and anisaldehyde, it is desirable to reduce the time of reaction and so check hydrolysis. A solution of sodium ethoxide (1.3 g. of sodium) in alcohol (25 c.c.) was added in one lot to a solution of benzoylmandelonitrile (12 g.) and anisaldehyde (11 g.) in alcohol (30 c.c.). Rise of temperature was checked by shaking the reaction mixture in running water, and after 7 minutes the material was extracted by addition of ether and water. After removal of the solvent, the residual liquor was treated with methyl alcohol and light petroleum. Cooling in ice and salt gave crystals which, once recrystallised from alcohol, weighed 0.9 g. and melted between 118° and 120°. These were identical with the original specimen (Greene and Robinson, *loc. cit.*) (Found: MeO, 7.9, 8.1. Calc. for  $C_{22}H_{18}O_4$ , MeO, 9.0%).

*Abnormal Production of Benzoylbenzoin.*—On three occasions when  $\frac{1}{2}$  mol. of sodium ethoxide was added drop by drop to alcoholic

solutions of benzoyl-*p*-methoxymandelonitrile and benzaldehyde, small quantities of benzoylbenzoin were obtained in a good state of purity. This unexpected result was ascertained in one case by combustion and the method of mixed melting point and in the others by the latter method only. The characteristic prismatic rods of benzoylbenzoin were also readily recognisable under the microscope. The yields of this product, starting in each case from 11.5 g. of benzoyl-*p*-methoxymandelonitrile and 11 g. of benzaldehyde, were 1.6 g. (m. p. 122—125°), 0.7 g. (m. p. 120—123°), and 0.6 g. (m. p. 119—122°), respectively. The condensation of benzoyl-*p*-methoxymandelonitrile with anisaldehyde does not afford a convenient means of preparing benzoylanisoin.

*4'-Methoxybenzoylbenzoin* (V; m. p. 127—128°).—A solution of sodium ethoxide (1.15 g. of sodium) in ethyl alcohol (30 c.c.) was added in one portion to benzoylmandelonitrile (23 g.) and anisaldehyde (22.5 g.) dissolved in ethyl alcohol (30 c.c.). The mixture was shaken in running water for 5 minutes and then worked up in the usual manner. The crystals (3.4 g.) which separated from the ether, recrystallised from 90% alcohol (75 c.c.), had m. p. 125—127°. The ethereal mother-liquor was treated as usual, and the crop recovered from the drying agent (magnesium sulphate) by addition of water, on recrystallisation, gave 4.9 g. of m. p. 124—127°; from the ethereal solution 2.4 g. of m. p. 121—124° were obtained. The pure product melted at 127—128° (Found: C, 76.1; H, 5.3; MeO, 8.5.  $C_{22}H_{18}O_4$  requires C, 76.3; H, 5.2; MeO, 9.0%). A mixture with the isomeride described above melted at 100—104°. *4'*-Methoxybenzoylbenzoin crystallises from alcohol or ether in colourless, prismatic rods and dissolves in cold concentrated sulphuric acid to a brassy yellow solution which, on warming, remains yellow for a time and then suddenly passes through reddish-brown to dark greenish-brown.

A further illustration of the sensitive nature of the general reaction was provided by an experiment in which a cold solution of sodium ethoxide (0.6 g. of sodium) in alcohol (25 c.c.) was, during 3 or 4 hours, gradually added to a cold solution of benzoylmandelonitrile (12 g.) and anisaldehyde (11 g.) in ethyl alcohol (30 c.c.). Some crystals separated during the course of the reaction, which was controlled by water cooling. These were filtered off, washed with water and alcohol, and recrystallised from alcohol. The substance (0.1 g.) had m. p. 120—124°, which was raised to 120—126° by admixture with *4'*-methoxybenzoylbenzoin and depressed by admixture with the other isomeride. The filtrate of the reaction mixture was extracted as usual and gave a syrup from which, by ~~recrystallisation~~, *4*-methoxybenzoylbenzoin (0.3 g.) was obtained.



*Piperonyl- $\alpha$ -furylcarbinyl Benzoate* (III).—This substance was obtained from benzoylmethylenedioxymandelonitrile (28 g.) and furfuraldehyde (23 g.) in alcohol (30 c.c.) by addition in one lot of a solution of sodium ethoxide (1.15 g. of sodium) in ethyl alcohol (30 c.c.). The mixture was shaken in running water for 5 minutes and then extracted as in other cases. From the ethereal solution, a crop was obtained which, after one recrystallisation from 90% alcohol (45 c.c.), gave 3.3 g. of crystals, m. p. 130—132°. A smaller fraction (1.3 g.), m. p. 117—130°, was recovered from the drying agent. In two half-scale experiments the yields were 1.4 g. of m. p. 125—130° and 1.6 g. of m. p. 125—129°. In the former, the reaction was allowed to proceed for 20 minutes before extraction, and this delay seems to have decreased the yield. Increase of the proportion of sodium to 1.1 g. for 14.1 g. of nitrile in a reaction which lasted 15 minutes led to the isolation of an impure product (3.4 g.), m. p. 103—106°.

From the three earlier experiments were obtained 6.6 g. of material, m. p. 131.5—133.5°, and for analysis a portion of this was recrystallised from glacial acetic acid, toluene and rectified spirit. The pure product melted at 132.5—133.5° (Found: C, 68.5; H, 4.1.  $C_{20}H_{14}O_6$  requires C, 68.6; H, 4.0%). The substance crystallised from alcohol in colourless, prismatic rods and when mixed with its isomeride of m. p. 140—141°, melted at 110—115°.

*$\alpha$ -Furoylpiperonylcarbinyl Benzoate* (IV).—This substance was prepared readily and in good yield by the condensation of piperonal (12 g.) with benzoylfurfuraldehydecyanohydrin (11 g.) in ethyl alcohol (40 c.c.). Sodium ethoxide (0.6 g. of sodium) in ethyl alcohol (20 c.c.) was added in one portion and the mixture was shaken in running water. After 25 minutes, the solid was collected, and only a minute quantity was recovered from the mother-liquor. The substance was recrystallised from glacial acetic acid (25 c.c.) and from ethyl alcohol (80 c.c.), and the main crop (4.7 g.) had m. p. 136—138°. For analysis, this material was recrystallised from alcohol, glacial acetic acid, 90% alcohol, toluene, and 90% alcohol, giving 3.1 g. of the pure substance, m. p. 140—141° (Found: C, 68.8; H, 4.1.  $C_{20}H_{14}O_6$  requires C, 68.6; H, 4.0%). The colourless, hexagonal plates dissolve in cold concentrated sulphuric acid to an intense crimson solution tinged with brown.

3:4- and 3':4'-*Methylenedioxybenzoylbenzoins* (I and II).—By reducing the time of reaction hydrolysis has been lessened and more convenient methods of preparing these isomerides are now submitted.

A solution of sodium ethoxide (0.6 g. of sodium) in ethyl alcohol (20 c.c.) was added to benzoylmandelonitrile (12 g.) and piperonal (11 g.) in ethyl alcohol (40 c.c.). The mixture was shaken in

running water for 15 minutes and extracted with ether. The solid residue was crystallised from glacial acetic acid, giving 2.6 g. of material, m. p. 132.5—134.5°, and 1.1 g., m. p. 129—132°. The ethereal solution after the usual treatment gave 1.9 g. of crystals, m. p. 127—131°. A portion of this product, recrystallised once, was identical with authentic 3':4'-methylenedioxybenzoylbenzoin, m. p. 134—135°.

From benzoylmethylenedioxymandelonitrile (14.1 g.) and benzaldehyde (11 g.) dissolved in alcohol (40 c.c.) there were obtained, by addition, in one portion, of a solution of sodium ethoxide (0.6 g. of sodium) in alcohol (20 c.c.), 1.1 g. of a product, m. p. 144—147°, and 146—148° when mixed with 3:4-methylenedioxybenzoylbenzoin (m. p. 147.5—148.5°). In this experiment, the reaction was allowed to continue for 35 minutes.

When the time of reaction and the quantities of nitrile and aldehyde (but not of sodium) were halved, the percentage yield was almost doubled.

This work was carried out at the Universities of St. Andrews and Manchester. The author takes this opportunity of thanking Prof. R. Robinson, F.R.S., for his interest in it, and also the Carnegie Trustees for the award of a scholarship.

WELLCOME TROPICAL RESEARCH LABORATORIES,  
KHARTOUM, SUDAN.

[Received, June 11th, 1925.]

#### XLIV.—*The Reaction between Hydroxylamine and Ferric Chloride.*

By ALEC DUNCAN MITCHELL.

HYDROXYLAMINE is a compound of great interest from several points of view. Many years ago Haber showed (*Ber.*, 1896, 29, 2444) that it would oxidise ferrous salts in alkaline solution or suspension, and reduce ferric salts in acid solution, and he suggested that its structure in the two cases might be represented as  $H_3N \cdot O$  and  $H_2N \cdot OH$  respectively. The existence of such dynamic isomerides would account for the above behaviour, which is typical of many of the reactions of hydroxylamine, and, with the object of seeking a further basis for this hypothesis, the author has carried out several kinetic studies, since similar investigations have afforded such evidence in other cases (Mitchell, J., 1923, 123, 629, 2241).

The reactions of hydroxylamine are all very complicated, and, up to the present, only one, the subject of this communication, has been interpreted. It may be stated at once that, possibly because

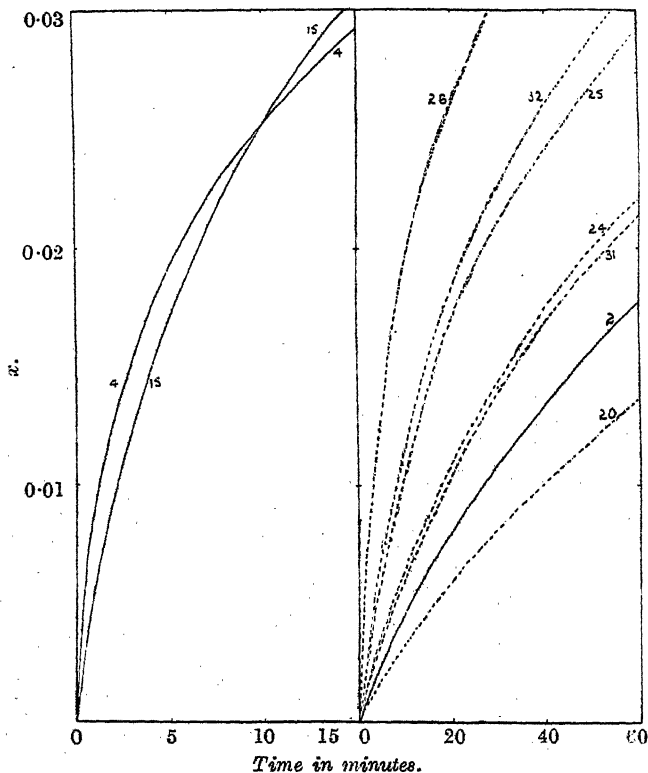
the acidic solutions involved may exclude one isomeride, the results have no bearing on the main problem, but they are of interest in other respects.

A kinetic study of the reactions of hydroxylamine appeared desirable in that no such examination has hitherto been made. A survey of the literature discloses more than twenty reactions in which the ultimate products have been studied, but the mechanism underlying their formation has usually been ignored. There are two partial exceptions to this statement: (1) Raschig ("Schwefel- und Stickstoff-Studien," 1924) studied the stoichiometrical ratios obtaining at various stages in the course of certain reactions, but did not investigate them kinetically; and (2) Brönsted (*Z. physikal. Chem.*, 1922, **102**, 187) made a rough colorimetric estimate of the effect of a saline solution on the reaction now discussed, and, from the apparent absence of appreciable "salt effect," concluded that reaction takes place between the metallic ion and undissociated hydroxylamine molecule to form a "critical complex." As will be seen later, however, the more accurate method used here indicates a definite negative salt effect (p. 347).

There seemed to be two difficulties in the way of the proposed investigations: (1) few of the reactions proceed quantitatively in one direction, the majority giving varying proportions of by-products, and (2) hydroxylamine reacts more or less readily with most of the reagents which might normally be employed in the estimation of the second reactant or the products. The second difficulty has been obviated in the present instance by analytical methods which are described in the experimental portion of this communication. The first difficulty has been minimised by choosing reactions, such as that under discussion, which appear to give but little by-product. In the present case, the reaction is quantitative under the conditions laid down by Raschig (*Annalen*, 1887, **241**, 190)—considerable excess of ferric salt and of sulphuric acid, and at least five minutes' boiling. These conditions could not, for various reasons, be applied in the present research, but it is believed that the necessary departures from them involve only slight errors. There is no doubt that the difficulties which had to be overcome by Raschig were the slowness of the reaction in its later stages and the possible persistence of an intermediate product. The former difficulty is immaterial in an investigation such as this, and the latter is only of importance in so far as it affects analysis, but the method used is believed to eliminate this effect (p. 346). A consideration of the work of Bray (*J. Amer. Chem. Soc.*, 1919, **41**, 1363) in conjunction with that of Kurtenacker and Neusser (*Z. anorg. Chem.*, 1923, **131**, 27) shows that, using only a bare excess of ferric salt, reaction is incomplete

simply because it becomes extremely slow, and that, using neutral or very feebly acidic solutions, there is slight formation of elementary nitrogen, corresponding to 4%, at most, of the hydroxylamine. Apart from this, these authors find no evidence of side-reactions, and it would therefore appear that the departures from the prescribed conditions do not materially affect the present research. The author's experience confirms the production of traces of nitrogen

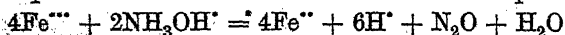
FIG. 1.



in the least acidic solutions, and also indicates that, under the conditions which are imposed upon this research—restrictions which often necessarily obtain in kinetic studies—traces of higher oxides of nitrogen are produced (p. 346).

#### *Mechanism of the Reaction.*

The complete reaction under ideal conditions is represented by



and the molar concentrations of the first four species will be repre-

sented by  $a$ ,  $b/2$ ,  $f$ , and  $h$  respectively. It will be seen that, if the suffix 0 represent these at zero-time, and the suffix  $t$  at any specified time corresponding to the reduction of  $x$  moles of ferric iron, then  $a_t = a_0 - x$ ,  $b_t = b_0 - x$ ,  $f_t = f_0 + x$ , and  $h_t = h_0 + 3x/2$ .

A few experiments using ferric chloride and hydroxylamine hydrochloride led to no conclusion as to the order of the reaction. The initial velocity was enormous, but was damped down so rapidly that, unless a reaction of about the tenth order was assumed, one had to ascribe repressing effects to one or more of the products of reaction. Even when the velocity became of a lower order, a reduction of, say, 5%, in the concentrations of ferric iron and hydroxylamine caused the velocity to be reduced to one-half or less (see Expt. 1 as an example). (The reduction of cupric salts by hydroxylamine in the presence of acetic acid and sodium acetate is found to be similar in this respect.)

The initial addition of hydrochloric acid produced much slower reactions, but the damping was still so marked that a second product of reaction was suspected of a repressing effect (see Fig. 1, Expt. 4). Initial addition of ferrous salts also produced a great depression in velocity whether hydrochloric acid had been added or not. (The effects of equi-molar additions of hydrochloric acid or ferrous salts were not quite the same.) When both hydrochloric acid and ferrous salts were present in fair concentration, the reaction was closely termolecular—bimolecular with regard to ferric iron and unimolecular with respect to hydroxylamine. The termolecular velocity coefficient fell off slightly, but this was provisionally attributed to the progressive accumulation of ferrous and hydrogen ions, as reaction in the presence of a large excess of both was too slow for a more rigid test to be practicable. No other type of ordinary velocity coefficient gave any approach to constancy.\*

\* In this connexion may be mentioned an interesting instance of the danger of relying on initial velocities from a few isolated experiments as a clue to the order of reaction: in a few runs with initial hydrochloric acid and hydroxylamine kept constant, the apparent initial velocity (that based on the gross change before the first titration) was roughly proportional to the initial concentration of ferric chloride, which was varied, and the erroneous deduction was drawn that this was involved to only the first order. The explanation is due to the fact that, as will be seen later, the velocity in these experiments is inversely proportional to the concentration of ferrous iron, so that  $\delta x \propto a^2/f$ ; since  $f$  increases from zero to  $\delta x$  in the small interval concerned, its mean concentration is  $\delta x/2$ , so that  $\delta x \propto a^2/\delta x/2$  as an approximation, or  $(\delta x)^2 \propto a^2$  or  $\delta x \propto a$ —thus accounting for the erroneous conclusion. Strictly, one is dealing with an integral summation starting with an infinite velocity for an infinitely short time, but actually the velocity is of a measurable order almost instantly, so that the approximation involved here is sufficiently near the truth to account for the observed facts.

The effects of the products of the reaction in repressing it indicated an equilibrium as an *intermediate* stage in the reaction; and it could be *only an intermediate stage* because the reaction goes to completion, forming the basis of Raschig's method for the estimation of hydroxylamine, so that the ultimate products could not reverse the reaction.

Further evidence bearing on the equilibrium was obtained when certain experiments, the early stages of which were too rapid for detailed measurement at 25°, were carried out at 15.5°. Seven experiments, of various types, all gave the temperature coefficient of 5.9 for 9.5°, which, by exponential proportion, becomes 6.5 for 10°. Just as temperature coefficients of less than unity—or negative coefficients as they would be if expressed more rationally—are interpreted as evidence of intermediate compounds (Eggert, *Z. Elektrochem.*, 1921, 27, 455, and Skrabal, *ibid.*, 1915, 21, 461, on the Landolt reaction, and Hasche and Patrick, *J. Amer. Chem. Soc.*, 1925, 47, 1214, on the reaction between nitric oxide and oxygen), so this abnormally high temperature coefficient is regarded as indicating the existence of an intermediate equilibrium, which is displaced, by a rise in temperature, in a direction more favourable to reaction, this accelerating effect being superimposed upon the normal temperature effect.

No attempt has been made to correct for incomplete ionisation of electrolytes; the corrections which have been made for salt effect (p. 349) in certain cases tend to make a rough correction of this kind, however, and serve to make experiments more comparable.

The recognised methods of treating reaction velocities fail where the indications are that the initial velocity is infinite or of a very high magnitude. It was therefore necessary to obtain expressions, even if they were empirical, which would represent the course of the reaction, before one could draw any conclusions of a quantitative nature, and subsequently a certain amount of theoretical justification was found for them. As a tentative expression the following was used:

$$\frac{dx}{dt} = k_1 \frac{(a-x)^2(b-x)}{(h+3x/2)(f+x)} \quad \dots \dots (1)^*$$

It is here necessary for the purposes of discussion to classify experiments into four types as follows:

(I) Those having only ferric chloride and hydroxylamine hydrochloride initially.

(II) Those having additional hydrochloric acid alone initially.

(III) Those having additional ferrous iron alone initially.

\* The integrals of all the formulæ used here are very cumbersome and their solutions are tedious, so details are omitted.

(IV). Those having both additional hydrochloric acid and ferrous iron initially.

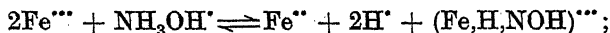
Expression (1) gave for all experiments, except those of type (I), values for  $k_1$  which were reasonably constant in any one experiment, as is shown for two types by Expts. 5 and 18. The values showed a slight tendency to fall as a rule, and, as will be seen in the table, varied from one experiment to another in such a way as to suggest that the second power of  $(h + 3x/2)$  should replace the first power. When this amended expression

$$\frac{dx}{dt} = k_2 \frac{(a - x)^2(b - x)}{(h + 3x/2)^2(f + x)} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

is applied to the experiments the results are as shown in the same table. In this table, the values of  $a$ ,  $b$ ,  $f$ , and  $h$  are expressed in moles per litre and relate to initial conditions; the values of  $k_1$  and  $k_2$  as found from the differential determinations of velocity (see p. 347) are shown as well as those obtained by integration: the latter often obscure marked drifts towards the end of a reaction and thus are not so trustworthy in these circumstances as the differential values, although they are far less subject to experimental error. In experiments of types (I), (II), and (III), where the initial velocity is very great, the integrated values are a more trustworthy guide as to the course of the early stages of the reaction. Although  $k_2$  shows a rise throughout every reaction, it is noteworthy that its order of magnitude is very consistent throughout the whole range of experiments, which cover a wide variety of conditions and are usually continued until over 50% of the possible reaction is completed—this extent is indicated for each experiment in the column “% completed.” As it was highly improbable that this consistency was a mere coincidence, a search was made for a theoretical basis which would account for the general agreement and possibly afford a reason for the anomalies noticed.

If the hypothetical nitroxyl were produced according to the equation  $2\text{Fe}^{+++} + \text{NH}_2\text{OH} \rightleftharpoons 2\text{Fe}^{++} + 3\text{H}^+ + \text{HNO}$  (and subsequently decomposed to nitrous oxide), this would be expected to play a part in the repression of the reaction, and the effect of ferrous and hydrogen ions would be more nearly in proportion to the second and third powers of their respective concentrations. As a matter of fact, the introduction into the formulæ of any function of  $x$ , giving, for example,  $dx/dt = ka^2b/hfx$  or  $dx/dt = ka^2b/h^2fx$ , renders them quite incapable of representing the course of reaction; and the use of the second or third powers of  $f$  or  $h$  respectively is similarly useless. The absence from (2) of any term representing an intermediate compound seems to be capable of explanation as follows.

One has circumstantial evidence for assuming the formation of a complex, thus :



denoting the complex by  $M$  and its concentration by  $m$ , and assuming it to decompose to nitrous oxide according to a unimolecular law, we have for the rate of accumulation of  $M$  :

$$dm/dt = k_3 a^2 b - k_4 h^2 f m - k_5 m \quad . \quad . \quad . \quad (3)$$

and for the rate of diminution of ferric iron :

$$dx/dt = k_3 a^2 b - k_4 h^2 f m = dm/dt + k_5 m \quad . \quad . \quad . \quad (4)$$

(If one deals with the very early stages of reaction, it would be necessary to allow for the fact that a certain amount of hydrogen and ferrous ions is locked up in the complex  $M$ , and is therefore present as such in a concentration less by an amount  $m$  than the values  $(h + 3x/2)$  and  $(f + x)$ ; the error involved by ignoring this is small when  $h_0$  and  $f_0$  are finite, however, and the equations would become extremely complicated.)

After the very early stages of a reaction,  $m$  tends to keep nearly constant, owing to a compensating effect of the three reactions tending to adjust it; one would then have  $dm/dt = 0$ , and  $dx/dt = k_5 m = k_3 a^2 b - k_4 h^2 f m$ . Solving for  $m$  and substituting, one has

$$dx/dt = k_3 k_5 a^2 b / (k_4 h^2 f + k_5) \quad . \quad . \quad . \quad (5)$$

When both  $h_0$  and  $f_0$  are zero,  $dx/dt = k_3 a^2 b$ , independently of any simplifying assumptions, and, since reaction is so rapid, it is certain that  $k_3$  must be very large. Such a condition only obtains in the initial stages, to which expression (5) does not apply, owing to the nature of the assumptions made. The term  $k_4 h^2 f$  in experiments of types (II) and (III) rapidly becomes of a finite order, and in type (IV) is already of a finite order, so that, as soon as  $k_4 h^2 f$  becomes markedly greater than  $k_5$ , one arrives at the same expression as was obtained empirically,  $k_3 k_5 / k_4$  being equal to  $k_2$  in (2). The expressions (3) and (4) are too complicated for complete solution, so that one is unable to find whether they would account for the rise in the value of  $k_2$  or for certain other discrepancies to be discussed later.

It is possible that reaction involves the free undissociated basic molecule:  $2\text{Fe}^{+++} + \text{NH}_3\text{OH} \rightleftharpoons \text{Fe}^{++} + \text{H}^+ + (\text{NOH}, \text{Fe}, \text{H})^{+++}$ . This mechanism would lead to an expression such as (1) but the term  $(b - x)$  would have to be corrected in order to make it correspond to the free base. After the hydrogen-ion concentration reaches a value which is very early attained in experiments of types (I) and (III) and which obtains initially in the other types, this corrected



term becomes approximately  $(b - x)k_h/(h + 3x/2)$ ,  $k_h$  being the hydrolytic dissociation constant of hydroxylamine hydrochloride. An expression similar to (2) therefore results, and, as this expression is not applicable to the early stages, a decision between this possibility and that developed above cannot be made. It is believed, however, that the extremely rapid fall in the initial concentration of free basic molecules in experiments of types (I) and (III) would require an even greater fall in velocity than is actually found, so that the foregoing hypothesis is preferred.

### *Discussion of Results.*

An apparent anomaly is exhibited by Expts. 15 and 23 in type (III), since  $k_1$  rises at first in these cases but falls as a rule, and in this type alone  $k_2$  appears to be zero initially. The latter fact is immaterial in view of the way in which  $k_2$  is derived on theoretical grounds, and it cannot be expected to hold at  $t = 0$ . The fact that  $k_1$  exhibited a different behaviour in these experiments from the more usual behaviour is connected with the circumstance that initial ferrous iron depresses more than initial equi-molar hydrogen ions, as is shown by the curves for Expts. 4 and 15 (Fig. 1), Expts. 22 and 23 being similar. In each case, however, as the curves show, the experiment with more ferrous iron overtakes the other as hydrogen ions accumulate during the progress of the reaction, and then one has the conditions which prevail in type (IV), where hydrogen ions depress to a greater extent than the equi-molar ferrous ions—see Expts. 17 and 18 or 13 and 14. All these peculiarities become normal when one considers the way in which  $(h_0 + 3x/2)(f_0 + x)$  varies differently with increase in  $x$  according as  $h_0$  or  $f_0$  is zero or both finite, and are due ultimately to the fact that the functions of hydrogen ions and ferrous ions in repressing the reaction are different.

There still remains the interesting fact that, even after corrections have been made for salt effect (p. 349), experiments in which ferrous iron is added initially seem to give slightly lower values for  $k_2$  with increasing amounts of ferrous iron. No satisfactory explanation has been found for this behaviour. On the other hand, both  $k_1$  and  $k_2$  are far more satisfactory in experiments in which there is no initial ferrous iron (type II) than in those where there is no initial acid (type III), so that the equations used appear to be more satisfactory for relatively rapid increases of ferrous iron than of hydrogen ions.

With the object of gaining further insight into the mechanism and of obtaining an estimate of the extent to which hydrogen and ferrous ions are diminished owing to the existence of the complex,

six experiments were devised so as to correspond with the various conditions which might obtain in Expt. 2 after it had reached a certain stage. Initially it had  $\alpha = 0.200$ ,  $b/2 = 0.100$ , and the stage chosen was when 0.075 of the ferric iron had been reduced. At this stage, which was attained in 29.5 minutes, one would have  $h = 0.075 \times 3/2$  and  $f = 0.075$  if 3 and 2 atoms of hydrogen and iron respectively remained free in solution according to the stoicheiometric equation. The six experiments were chosen with the above values of  $\alpha$  and  $b$  and with concentrations of  $h$  and  $f$  as shown:

Expt.	$h$ .	$f$ .				
20	0.1125	0.0750	corresponding to	3H <sup>+</sup>	and 2Fe <sup>2+</sup>	remaining free.
24	0.0750	0.0750	" "	2H <sup>+</sup>	" 2Fe <sup>2+</sup>	" "
25	0.0750	0.0375	" "	2H <sup>+</sup>	" Fe <sup>2+</sup>	" "
26	0.0375	0.0375	" "	H <sup>+</sup>	" Fe <sup>2+</sup>	" "
31	0.1125	0.0375	" "	3H <sup>+</sup>	" Fe <sup>2+</sup>	" "
32	0.0375	0.0750	" "	H <sup>+</sup>	" 2Fe <sup>2+</sup>	" "

As can be seen from the curves \* (Fig. 1), the initial velocities are slower in the case of Expt. 20, and faster in all the others, than the reaction from the corresponding point in Expt. 2, the curve in the case of this experiment being plotted with the origin corresponding to the stage concerned. This would indicate that in Expt. 2 there are fewer hydrogen and ferrous ions opposing reaction than in Expt. 20, some being locked up in the complex. On the other hand, in Expt. 2 the complex is already at the concentration imposed by the stabilising effect of the reactions affecting it, whereas, in the earliest stages of the other reactions, it has probably not attained such a condition, so that comparisons are not rigid. Passing to the general course of the curves, it would appear that the conditions in Expt. 2 are such as would be expected from the repressing effect of approximately 2.7 moles of hydrogen ion and 1.7 moles of ferrous ion, for, considering the various values of  $t$  for constant values of  $x$  (which is the correct criterion), its curve is slightly farther from that of Expt. 20 than from a compromise between those of Expts. 24 and 31 which would approximately represent 2.5 and 1.5 moles respectively; as it is also about one-third of the way between those of Expts. 20 and 25, it would appear to correspond to 2.67 and 1.67 moles of hydrogen and ferrous ions respectively; both situations suggest that only about one-third of the hydrogen and ferrous ions which might possibly be locked up in the complex are actually so, or, that two-thirds of the total complex formed have already broken down to final products.

Although the results in the foregoing discussion leave many details

\* In these curves the extent of reduction ( $x$ ) is plotted against time ( $t$ ) which has been reduced in accordance with the correction for salt effect (p. 349).

in an unsatisfactory state, there is little doubt that the general conclusions are not far from the truth, and it is therefore of interest to compare them with certain other workers' views.

Raschig's ideas on the general course of the oxidation of hydroxylamine are put forward in detail in his "Stickstoff- und Schwefel-Studien," 1924. They are, briefly, that the first stage consists in the slow formation of the radical  $\text{NH}\cdot\text{OH}$ , which unites with a similar radical to give  $\begin{array}{c} \text{H}\cdot\text{N}\cdot\text{OH} \\ || \\ \text{H}\cdot\text{N}\cdot\text{OH} \end{array}$ . After this point a variety

of possibilities is supposed to arise and the persistence of any one type of molecule will depend not only on its inherent stability but also on the rapidity with which it may be further oxidised. Thus,

in the next phase one might have  $\begin{array}{c} \text{N}\cdot\text{OH} \\ || \\ \text{N}\cdot\text{OH} \end{array}$  or  $\begin{array}{c} \text{H}\cdot\text{N} \\ | \\ \text{H}\cdot\text{N} \end{array} > \text{O}$  according as

the dihydroxyhydrazine could be further oxidised before it dehydrated or not, and in the latter case further oxidation would give hyponitrous acid,  $\begin{array}{c} \text{H}\cdot\text{N} \\ | \\ \text{HO}\cdot\text{N} \end{array} > \text{O}$ , which would decompose to nitrous

oxide, if nothing were present to oxidise it more rapidly than it could decompose. These views appear to the author to have the great advantage that they explain the variety and varying proportions of the end-products.

The results described herein, however, indicate that the first measurable stage involves, in effect, the removal of two hydrogen atoms from each molecule of hydroxylamine, because undoubtedly two molecules of ferric salt are implicated, and it is difficult to see what (if any) preliminary rapid reaction, save the formation of a "critical complex," could lead to a subsequent measurable termolecular reaction. The molecule thus appears to be oxidised to the stage represented by the hypothetical nitroxyl or nitrous oxide, although the latter is only produced as the result of secondary changes. These views agree, to a certain extent, with the earlier opinion expressed by Raschig, when dealing with the estimation of hydroxylamine by ferric salts, that an intermediate compound (possibly nitroxyl) of moderate stability is produced, which delays the completion of the reaction for analytical purposes (*Z. angew. Chem.*, 1904, 17, 1411).

As will be seen from the experimental portion of this paper, there is no foundation for Brönsted's statement, quoted on p. 337, that the reaction under discussion is not appreciably susceptible to salt effect, although the magnitude is not so great as he appeared to look for. Actually there is a definite negative salt effect, which would, according to Brönsted, indicate reaction between ions of opposite polarity; but it is doubtful whether his hypotheses, which

are based on comparatively simple cases, can be extended to such complicated reactions as the present.

The hydroxylamine was always employed as hydrochloride, which had been recrystallised and freed from excess acid; both this salt and the ferric chloride would give a trace of free hydrochloric acid by hydrolysis, so that, in experiments with no added acid, there would always be a trace of free acid initially, which would slightly affect the earliest velocity coefficients.

#### EXPERIMENTAL.

All the experiments were carried out at 25°, with the exception of those necessary to find the temperature coefficient. Time is expressed in minutes throughout. The details call for no special description except in regard to the analytical method. The course of the reaction was followed by the estimation of unchanged ferric iron. The process was based on two facts: (1) hydroxylamine has no effect on iodine during the short time necessary for titrations provided that considerable mineral acid is present—sulphuric acid sufficient to be in normal concentration throughout the titration was found to fulfil this condition; and (2) ferric iron can be estimated consistently and fairly accurately by titration of iodine liberated from potassium iodide, if a trace of cuprous iodide is present as recommended by Hahn and Windisch (*Ber.*, 1923, 56, 598). The equilibrium which tends to be set up ( $\text{Fe}^{+++} + \text{I}' \rightleftharpoons \text{Fe}^{++} + \text{I}$ ) is displaced by titration of iodine as fast as it is formed, and the presence of the cuprous salt accelerates the reaction (presumably by more rapid reduction of ferric salt and continuous re-formation of cuprous salt) to such an extent that titrations can be completed in the ordinary time instead of lasting for several minutes, as in the absence of cuprous salt. Although the method has been criticised (Rupp, *Apothek. Z.*, 1924, 39, 422), the author's experience is that it is useful and gives results about 1 part in 300 parts high (with titres of 40 c.c.), but this error might be reduced if precautions were taken against the aerial oxidation of the solution containing hydriodic acid and ferrous salts.

The starch-iodine coloration returns after a few minutes in the titrations made during actual runs, and rather less rapidly in controls with ferric salts in the absence of reaction products. The difference is attributed to the presence of traces of nitrous acid.

As the result of many duplicate runs, it may be stated that experiments are reproducible almost invariably within about 0.1 c.c. on titres of usually 30 or 40 c.c.

The behaviour of a complex of the type suggested on p. 342 in such titrations is, of course, uncertain; it might react either as

ferrous or as ferric iron. The latter possibility is improbable, for the apparent rate of initial change would then be far less than the actual, and would subsequently tend to increase temporarily as the complex broke down; the apparent course of the reaction shows such enormous diminution in velocity that it is more likely that the complex reacts as a ferrous compound.

A control was made to ascertain whether hydroxylamine in nearly neutral solution exercised any oxidising effect on ferrous iron, such as it exerts in alkaline solution. The result was definitely negative.

The curves obtained by plotting experimental differential velocities against  $x$  change so rapidly that they are not capable of "smoothing." The velocities shown in the tables were therefore obtained by plotting  $x$  against the square-root or fourth-root of time, according to circumstances. The fairly flat curve thus obtained was smoothed and the values of  $\sqrt{t}$  or  $\sqrt[4]{t}$  corresponding to a series of values of  $x$  were read off, and, from the values thus obtained, a further curve was constructed, on the basis of  $v = \delta x / \delta t$ , showing the relation between  $x$  or  $(a - x)$  and  $v$ . Even this method leaves considerable uncertainty in the early stages of experiments of type I. The integrated velocity coefficients are based on unsmoothed values.

*Salt Effect.*—Experiments similar to No. 4 were made with the addition of  $M/10$ - and  $M/5$ -ammonium sulphate; they gave results uniformly slower in the proportion 1.14 and 1.30, respectively. A similar experiment comparable with No. 2 gave a slightly greater depression. The primary object of this type of experiment was to find what correction, if any, should be applied to experiments of types III and IV (in which the ferrous salt had been added, for convenience, as ferrous ammonium sulphate), in order that they should be comparable with one another and with those of other types. When a definite effect was found, it was essential to make a few other determinations in order to obtain an estimate of that due to ferrous sulphate. An experiment parallel with No. 12, but having  $M/10$ -ammonium sulphate present, in addition to the  $M/10$  already added as the double salt, showed a reduction of velocity in the ratio 1.17 to 1, whereas from the foregoing one would have expected a ratio of 1.30 to 1.14, i.e., 1.14 to 1—a result which is as near as can be expected from the graphical methods which have to be used in the absence of really satisfactory velocity coefficients, and which shows that the salt effect is fairly consistent.

$M/15$ -Aluminium sulphate gave a depression identical with that of  $M/5$ -ammonium sulphate and, therefore, twice as great as the  $M/10$ -ammonium sulphate to which it is equivalent; this result is characteristic of the ion of higher valency.

TABLE I.

< = values rising during expt.		> = values falling during expt.		$k_1 \times 10^3$		$k_2 \times 10^3$		% completed.
		(c) = approx. constant at value annotated.		Integrated.		Differential.		
Expt.	a.	b.	h.	f.	Integrated.	Differential.	Integrated.	Differential.
Type I.	1	0.200	0.0500	—	500 > 250	470 > 220	150 < 245	190 < 260
	2	"	0.1000	—	500 > 200	350 > 200 (c)	160 < 240	230 (c)
	3	0.100	0.0500	—	800 > 360	500 > 370 (c)	140 < 265	210 < 260
	4	0.200	0.0500	0.1000	—	164 > 120	140 (c)	180 < 220
Type II.	5	"	"	—	89 (c)	88 (c)	180 < 225	185 < 220
	6	0.100	"	0.2000	—	89 (c)	192 (c)	180 < 210
	7	0.200	"	0.8000	—	—	170 (c)	170 < 200
	8	0.100	"	0.2000	—	84 (c)	176 (c)	—
	9	"	0.0250	0.8000	—	—	192 (c)	—
	10	0.200	0.1000	0.8000	—	24 (c)	168 (c)	—
	11	0.040	0.0100	0.8000	—	21 (c)	160 < 240	180 < 240
	22	0.200	0.0500	0.0500	—	210 > 170	0 (?) < 200	115 < 230 (c)
Type III.	15	0.200	0.0500	0.1000	85 < 260 (c)	65 < 270 > 240	0 (?) < 215	200 < 255
	23	"	"	0.0500	220 < 290 > 250	320 > 215	200 < 230	170 < 230
	12	0.200	"	0.1000	169 (c)	145 (c)	150 < 182	210 < 250
	13	"	"	0.1000	140 (c)	97 (c)	195 < 220	110 < 195
	14	"	"	0.2000	97 (c)	200 > 140	171 < 215 (c)	165 < 240
	17	"	"	0.0500	195 > 170	150 > 130	145 < 210	150 < 215 (c)
	18	"	"	0.1000	148 (c)	240 > 155	170 < 190	195 < 260
	19	"	"	0.0500	240 > 180	138 (c)	170 < 220	190 < 290
Type IV.	20	0.125	0.0625	0.0750	140 (c)	220 > 185	192 < 260	180 < 255
	24	"	"	0.0750	205 (c)	220 > 190	195 < 245	200 < 265
	25	"	"	0.0750	222 > 200	310 > 220	200 < 250	145 < 230
	26	"	"	0.0375	330 > 260	155 (c)	120 < 200	—
	31	"	"	0.1125	155 (c)	255 > 220	—	—
	32	"	"	0.0375	250 (c)	—	—	—
	33	"	"	0.0750	260 (c)	—	—	—
	34	"	"	0.0750	—	—	—	—

Zinc ammonium sulphate was chosen as being best suited for comparison with the ferrous ammonium sulphate. For  $M/5$ - and  $M/10$ -solutions it showed depressions in the proportions 1.54 and 1.31 respectively. As these are consistent with the foregoing results, the general trend was adopted as the basis for corrections of all experiments of types III and IV, and the factors by which velocities are multiplied (or times divided) are :

for 0.2000 molar ferrous ammonium sulphate	1.54
0.1000    "    "    "    "	1.30
0.0750    "    "    "    "	1.22
0.0500    "    "    "    "	1.14
0.0375    "    "    "    "	1.11

A comparison of, for example, Expts. 10 and 11 does not indicate the relatively large salt effect which might be expected from a five-fold change in the concentration of the trivalent ferric salt, and, for this reason, no attempt has been made to correct for such salt effect.

Experiment I.  $a = 0.2000$ ,  $\frac{1}{2}b = 0.0500$ .

$t$ .	$x$ .	$v \times 10^5$ .	Integrated.		Differential.	
			$k_1 \times 10^5$ .	$k_2 \times 10^6$ .	$k_1 \times 10^5$ .	$k_2 \times 10^6$ .
*0.33	0.0212	—	510	122	—	—
*0.83	0.0274	900	489	151	468	193
*1.50	0.0316	500	450	162	385	180
*2.17	0.0348	370	437	180	378	198
*3.67	0.0390	260	402	185	375	219
5	0.0432	190	—	—	382	247
*9.7	0.0480	125	346	198	360	259
12	0.0516	80	—	—	300	232
*20	0.0556	55	313	210	275	230
21	0.0570	50	—	—	277	237
30.5	0.0604	37	284	206	262	237
45	0.0650	25	289	230	250	240
70	0.0700	16	273	236	232	244
140	0.0780	8	252	247	223	260
160	0.0794	—	246	245	—	—

Experiment 5.  $a = 0.2000$ ,  $\frac{1}{2}b = 0.0500$ ,  $h = 0.2000$ .

*0.52	0.0042	—	91	182	—	—
*1.7	0.0074	193	92	191	88	186
*4.3	0.0114	107	94	198	84	182
6	0.0126	94	—	—	85	184
*8.6	0.0146	77.5	(82)	(176)	86	191
13	0.0178	60	—	—	88	202
*21	0.0220	42.5	88	197	87	203
23	0.0228	40	—	—	88	205
*38	0.0280	27	90	206	86	210
54	0.0316	22	—	—	89	220
*59	0.0326	20.5	87	204	88	220
91	0.0380	14.5	—	208	87	225
170	0.0470	8	89	224	82	220
284	0.0544	—	85	234	—	—
410	0.0596	—	84	224	—	—

\* Indicates that these values are taken from an experiment at  $15.5^\circ$  and the time is corrected for the temperature coefficient.

Experiment 18.  $a = 0.0200$ ,  $\frac{1}{2}b = 0.0500$ ,  $h = 0.1000$ ,  $f = 0.0500$ .

(All values of  $v$ ,  $k_1$ , and  $k_2$  should be multiplied by 1.14, the salt effect factor.)

5	0.0048	82.5	142	162	134	143
12	0.0098	63.0	134	145	133	152
23	0.0158	47.0	134	152	134	165
39	0.0222	32.8	134	161	128	171
76	0.0316	20.3	129	163	126	185
110	0.0374	14.7	128	174	122	190
171	0.0448	10.0	125	182	119	199
255	0.0518	6.8	123	189	116	207
320	0.0557	5.4	122	190	114	209

(The product  $hf$  increases four-fold, and  $h^2f$  seven-fold during the run.)

### Summary.

1. The rate of reaction *after the early stages* is directly proportional to the concentration of hydroxylamine and to the square of that of ferric chloride, and inversely proportional to the concentration of ferrous salt and to the square of the hydrogen-ion concentration.

2. The most probable interpretation is that reaction proceeds by way of an intermediate equilibrium involving a complex of the type shown:  $2\text{Fe}^{+++} + \text{NH}_2\text{OH}^+ \rightleftharpoons \text{Fe}^{++} + 2\text{H}^+ + (\text{NOH}, \text{Fe}, \text{H})^{+++} \rightarrow \text{N}_2\text{O}$ , etc.

3. The abnormal temperature coefficient of 6.5 for a  $10^\circ$  rise would thus be partly due to a more favourable displacement of the equilibrium.

4. "Salt effect" is negative—reaction velocity is depressed by the addition of indifferent salts.

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## XLV.—The Structure of the Normal Monosaccharides. Part IV. Glucose.

By EDMUND LANGLEY HIRST.

IN Part I (Hirst and Purves, J., 1923, 123, 1352) the reasons which had led to the general adoption of a butylene oxide formula for normal aldose derivatives were reviewed, the need of more definite chemical evidence was pointed out, and a method for studying the problem was outlined which has since furnished strong evidence that normal derivatives of xylose (*loc. cit.*), arabinose (Hirst and Robertson, J., 1925, 127, 358), and rhamnose (Hirst and Macbeth, *this vol.*, p. 22) are, in fact, amyleno-oxidic and not butylene-oxidic, as hitherto been supposed. In the experiments now to be



described, the method has been extended to the hexose series. The oxidation of tetramethyl glucose, whose structural relationship to the normal methylglucosides and to glucose has been the subject of much investigation, has been studied and as a result it appears that the amylenoxide formula should be ascribed also to normal derivatives of glucose. This is in exact agreement with evidence as to the structure of glucose recently obtained by Charlton, Haworth, and Peat (this vol., p. 89), whose experiments were based on considerations of an entirely different nature. If this structure for glucose be accepted, changes in the nomenclature of certain derivatives will obviously be necessary analogous to the renaming of normal tetramethyl glucose as the 2:3:4:6- instead of the 2:3:5:6-derivative of glucose.

The principal method adopted in the present investigation was to oxidise tetramethyl glucose with nitric acid. The reaction between a normal trimethyl pentose (I) and nitric acid is simple in nature, involving only the oxidation to carboxyl of the reducing and the potential primary alcoholic groups situated respectively at the two ends of the pentose carbon chain. Trimethyl rhamnose (II) also reacted simply, the terminal group  $\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , produced by the action of the oxidising agent in forming trimethyl rhamnonic acid, giving quantitatively carboxyl and carbon dioxide. A methylated hexose, however, whether a 1:4- or a 1:5-oxide, presents a very different type of structure and it was to be expected that the course of oxidation would be more complicated. If the amylenoxide structure of tetramethyl glucose (III) be assumed, the first stage in the reaction would be the production of tetramethyl gluconic acid (IV), and its subsequent course would be determined by the action of nitric acid on the group  $\cdot\text{CH}(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OMe}$ , with the ketone  $\cdot\text{CH}(\text{OMe})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OMe}$  as a probable intermediate product. It is well known that ketones of the type  $\text{R}\cdot\text{CO}\cdot\text{R}'$  may be oxidised in different ways according to the experimental conditions. The main product from 2:3:4:6-tetramethyl glucose might therefore be either *d*-dimethoxysuccinic acid (V) or inactive xylotrimethoxyglutaric acid (VI), according as the break occurred between the 4th and 5th or between the 5th and 6th carbon atoms. It is evident that by a similar series of steps, shown in the accompanying scheme, butylene-oxidic tetramethyl glucose (VII) might also give dimethoxysuccinic acid, and it follows that the isolation of this acid alone would not enable precise conclusions to be drawn concerning the structure of tetramethyl glucose. The detection of xylotrimethoxyglutaric acid, on the other hand, would definitely indicate the presence of an amylenoxide linking. It was therefore necessary to establish experimental conditions such that the nature of the

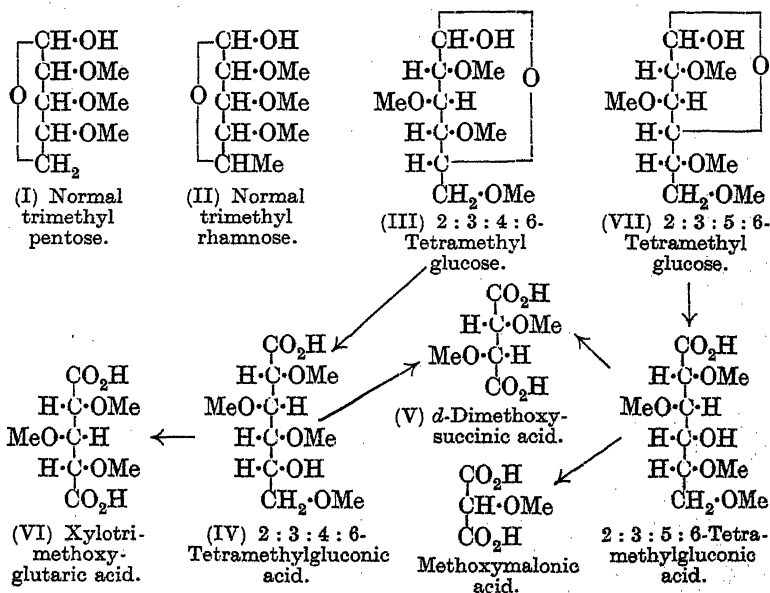
various oxidation products would lead definitely to the allocation of a structural formula.

This was ultimately accomplished by oxidising tetramethyl glucose for a short time with nitric acid of density 1.420. The reaction proceeded smoothly, was easy to control, and led to very little loss of material by side reactions. In this respect the reagent was much more satisfactory than the acid ( $d$  1.2) which had previously been most frequently employed in the sugar group. With the latter, even at comparatively low temperatures, the more prolonged action necessary to effect the requisite oxidation invariably yielded considerable quantities of oxalic acid by a profound decomposition of the molecule. The product isolated in good yield was a mixture containing both  $d$ -dimethoxysuccinic acid and xylotrimethoxyglutaric acid, which were separated from each other by taking advantage of the different rates of formation of their very characteristic crystalline diamides. Dimethoxysuccinamide (Purdie and Irvine, J., 1901, 79, 960) and xylotrimethoxyglutaramide (Hirst and Purves, *loc. cit.*) were thus obtained in a pure condition and their identity was placed beyond doubt by comparison with authentic specimens. It has already been indicated (Hirst and Macbeth, *loc. cit.*) that there appears to be no reason for suspecting any wandering of the methyl groups during oxidation, and it follows, therefore, from what has been said above, that normal tetramethyl glucose must be the 2 : 3 : 4 : 6-derivative possessing the amylene oxide formula (III); the possibility of a propylene or ethylene-oxide structure being entirely excluded by the nature of the products isolated.

The interest attached to this reaction and the desirability of accumulating as much evidence as possible concerning the oxidation of a fully methylated hexose led to a further study of the action of nitric acid and of alkaline potassium permanganate on tetramethyl glucose. The reaction appears to take an entirely different course from that of 2 : 3 : 6-trimethyl glucose when oxidised under precisely similar conditions (Irvine and Hirst, J., 1922, 121, 1222). The latter gave with nitric acid ( $d$  1.2) at 60° a dibasic acid (dimethylsaccharic acid), whereas tetramethyl glucose gives mainly tetramethylgluconic acid with a small quantity of dimethoxysuccinic acid, apparently without going through the intermediate stage of trimethylsaccharic acid. This difference is interesting, especially as butylene-oxidic trimethyl arabinose with a terminal group similar to that present in tetramethyl glucose can be oxidised to dimethoxyglutaric acid (Baker and Haworth, J., 1925, 127, 365). A sufficient number of examples has not, however, been examined to justify any views as to whether this behaviour is the exception or the rule. Prolonged treatment of tetramethyl glucose with nitric acid ( $d$  1.2)

at higher temperatures produces a complex mixture containing much oxalic acid and little or no trimethoxyglutaric acid, the chief constituent being dimethoxysuccinic acid. Oxidation with alkaline potassium permanganate gave oxalic acid and dimethoxysuccinic acid.

Summarising the evidence obtained from these experiments, it appears that the oxidation of amyleno-oxidic tetramethyl glucose with nitric acid leads first to 2:3:4:6-tetramethylgluconic acid. Further oxidation splits the carbon chain either between the 4th and 5th or between the 5th and 6th carbon atoms to give dimethoxysuccinic acid or xylotrimethoxy-glutaric acid, and the relative proportions in which the two changes take place vary with the experimental conditions, the latter change being favoured by oxidation with stronger acid for a shorter time.



#### EXPERIMENTAL.

*Stability of Dimethoxysuccinic Acid in Presence of Nitric Acid.*—Dimethoxysuccinic acid was heated in nitric acid (*d* 1.42) for several hours at 100°. No oxidation and no change in the initial specific rotation,  $[\alpha]_D + 69.5^\circ$  ( $c = 1.375$ ), were observed. Previous experiments have demonstrated the stability of trimethoxyglutaric acid.

*Oxidation of Tetramethyl Glucose with Nitric Acid* (*d* 1.42).—When a solution of tetramethyl glucose (5 g. of carefully recrystallised

material conforming to the accepted standards) in nitric acid (40 c.c.; *d* 1.42) was kept at room temperature, oxidation began after 5 minutes; thereafter the reaction was controlled by gradual heating in such a way that evolution of oxides of nitrogen never became rapid. After  $\frac{1}{2}$  hour, the temperature was raised to 90° and kept at this point for 2 hours; the evolution of gas had then almost ceased. Water (2 vols.) was added, and the excess of nitric acid removed by careful distillation at 40°/9 mm., with the addition of water in the usual manner. The dry oxidation product was a glass soluble with difficulty in methyl alcohol. It contained no oxalic acid. After esterification by boiling with methyl alcohol (50 c.c.) containing 4% of hydrogen chloride, the product was distilled under diminished pressure (for details of the method used, see previous papers). The main fraction (2.65 g.) was a colourless oil, b. p. 135–140°/10 mm. (bath at 150–155°),  $n_D^{20}$  1.4375. The first and last fractions (0.4 and 0.8 g., respectively) showed  $n_D^{20}$  1.4345 and 1.4416.

*Examination of the Oxidation Product.*—The main fraction was soluble in water and all the usual organic solvents.  $[\alpha]_D = +31.5^\circ$  in methyl alcohol (*c* = 2.085) and  $+33^\circ$  in aqueous ethyl alcohol (*c* = 0.8), and the characteristic change in rotation shown by lactones was not observed. The absence of lactonic substances was further shown by the compound titrating as an ester. The physical and chemical properties agreed most closely with those required for a mixture of 60% of methyl *d*-dimethoxysuccinate and 40% of methyl xylotrimethoxyglutarate (Found: C, 47.0; H, 7.05; OMe, 58.9; 0.106 g. required 9.0 c.c. of *N*/10-alkali for hydrolysis. Calc. for the above mixture: C, 47.2; H, 7.0; OMe, 60.9%; 9.5 c.c. The b. p., rotation, and refractive index are also in accord with this view. [Methyl *d*-dimethoxysuccinate has b. p. 135°/12 mm.,  $n_D^{20}$  1.4340,  $[\alpha]_D + 81^\circ$  in methyl alcohol (*c* = 6.26) (compare Purdie and Barbour, J., 1901, 79, 971), and methyl xylotrimethoxyglutarate has b. p. 132°/12 mm.,  $n_D^{20}$  1.4402, and is optically inactive.]

Complete confirmation of these views was obtained by the formation in good yield of crystalline dimethoxysuccinamide and xylotrimethoxyglutaramide by the action of ammonia on the mixed esters. A solution of 1.0 g. in 8 c.c. of methyl alcohol saturated with dry ammonia began, after a few hours, to deposit crystals in characteristic, opaque, white tufts. These were collected at the end of 3 days, and after being washed with alcohol and ether and dried at 105° were found to be pure dimethoxysuccinamide (yield 0.36 g.). The substance was insoluble in cold organic solvents, but slightly soluble in water, in which the value  $[\alpha]_D + 95^\circ$  (*c* = 0.80) was observed. It sublimed in long needles on being heated in a vacuum

(compare Purdie and Irvine, *loc. cit.*), showed no definite m. p., but when heated fairly quickly showed the following sequence of changes: darkened at about 245°, melted partly with decomposition at 269°, and was completely decomposed at 276° (Found: OMe, 34.3. Calc., OMe, 35.2%). Its properties were in exact agreement with those of an authentic specimen of the amide prepared from methyl *d*-dimethoxysuccinate.

The mother-liquor of the dimethoxysuccinamide was kept for a further 4 days. Colour changes took place similar to those observed during the formation of xylotrimethoxyglutaramide (*loc. cit.*), and 7 days from the beginning of the experiment another crop of crystals began to be deposited as flat, transparent prisms, resembling xylotrimethoxyglutaramide in crystalline form. After 12 days, 0.25 g. was collected. This material showed a moderate solubility in water and could be recrystallised from an alcohol-ether mixture. It was optically inactive (tested in 2% solution in water). It melted in air to give a dark blue liquid, m. p. 194–195°, and at 194–195° when mixed with an authentic specimen of the glutaramide prepared from xylose (Found: C, 43.5; H, 7.4; OMe, 41.1. Calc.: C, 43.6; H, 7.3; OMe, 42.3%).

Further quantities of dimethoxysuccinamide were obtained by treating with ammonia in methyl alcohol the first and the last fraction. No oxamide could be detected.

*Oxidation with Nitric Acid (d 1.2) at 75°*.—A solution of 5.5 g. of tetramethyl glucose in 85 c.c. of nitric acid (*d* 1.2) was heated at 75° for 12 hours until the reaction appeared to be complete. The oxidation products (isolated as before after esterification) were (a) methyl oxalate (1 g.), (b) a clear yellow syrup (3.5 g.), b. p. 138–149°/9 mm. (bath at 150–156°),  $n_D^{20}$  1.4415,  $[\alpha]_D + 54^\circ$  in alcohol ( $c = 1.348$ ),  $[\alpha]_D + 53^\circ$  in aqueous alcohol ( $c = 0.50$ ), decreasing to  $+43^\circ$ . This material on treatment with ammonia in methyl alcohol gave a small quantity of oxamide and much *d*-dimethoxysuccinamide. No xylotrimethoxyglutaric acid could be detected. The oxidation products under these conditions form a complex mixture, but consist principally of oxalic acid and dimethoxysuccinic acid. The high refractive index, the drop in rotation shown by the solution in aqueous alcohol, and the titration figures are in agreement with the view that some tetramethylgluconolactone was present in the main fraction (Found: C, 46.5; H, 6.6; OMe, 54.7%; 0.178 g. required 14.2 c.c. of *N*/10-alkali for hydrolysis, partly as lactone, partly as ester). The analysis of the corresponding lead salt is in accord with these views (Found: Pb, 50.0; OMe, 18.6%).

*Oxidation with Nitric Acid (d 1.2) at 60°*.—A solution of 7 g. of tetramethyl glucose in 50 c.c. of nitric acid (*d* 1.2) was heated at

85° until oxidation commenced, the temperature being then lowered to 60° and the reaction allowed to continue for 4½ hours. The product was treated in the way already described and was finally distilled. After a first fraction of 0.85 g., the greater part (4.0 g.) of the material was collected at 142–143°/9 mm. It could not be separated into its components by fractional distillation. The distillate was a neutral, clear syrup which developed acidity in contact with water;  $n_D^{20}$  1.4526,  $[\alpha]_D + 108^\circ$  in benzene ( $c = 1.176$ ). In water the initial value,  $[\alpha]_D + 80^\circ$  ( $c = 1.792$ ), dropped rapidly to 64° after 28 minutes, 54.5° after 83 minutes, 45° after 158 minutes, and 39° after 280 minutes; the final value was 35°. This behaviour is characteristic of  $\delta$ -lactones. Titration with alkali showed that the substance was partly lactonic and partly esteric in character. 0.1502 G. required (a) 5.0 c.c. of  $N/10$ -alkali as lactone, (b) 3.0 c.c. of  $N/10$ -alkali as ester (Found: C, 50.1; H, 7.5; OMe, 53.5%). 0.8 G. dissolved in 6 c.c. of methyl alcohol saturated with ammonia gave crystals of dimethoxysuccinamide (0.05 g.) in a few hours. These observations proved that the methyl ester of trimethoxysaccharolactone, if present at all, must have been there in very minute quantity, and the material under examination appeared to consist of 80% of tetramethylgluconolactone and 20% of methyl dimethoxysuccinate. This mixture requires C, 50.3; H, 7.5; OMe, 54.5% and 0.150 g. would require (a) 5.1 c.c. of  $N/10$ -alkali as lactone, (b) 2.9 c.c. of  $N/10$ -alkali as ester, whilst the b. p. and the initial and final values of  $[\alpha]_D$  are in agreement with those expected.

(For the properties of dimethoxysuccinic acid derivatives, see Purdie and Irvine, *loc. cit.*; for those of tetramethylgluconolactone, see Pryde, J., 1924, 125, 520; Charlton, Haworth, and Peat, *loc. cit.*)

*Oxidation with Potassium Permanganate.*—Tetramethyl glucose (5 g.) was dissolved in water (100 c.c.) rendered just alkaline with potassium hydroxide, and to the solution, heated at 75°, was added gradually potassium permanganate (25 g.) dissolved in hot water. The colour of the permanganate solution disappeared quickly at first, but very slowly towards the end. After filtering and passing carbon dioxide through the filtrate to remove free alkali, the solution was evaporated to small bulk at 50°/12 mm. The greater portion of the potassium was removed by means of perchloric acid and after elimination of the remaining water the product (partly free acid and partly potassium salt) was esterified with acid methyl alcohol. On isolating and distilling the ester, 0.6 g. was obtained as a first fraction. This was almost entirely methyl oxalate (the identity of which was confirmed by transforming it into oxamide). The main fraction

(2 g.) showed b. p. 130—135°/9 mm. (bath at 145°),  $n_D^{20}$  1.4342,  $[\alpha]_D + 43^\circ$  ( $c = 1.68$ ) in methyl alcohol [Found: OMe, 55.5; CO<sub>2</sub>Me (by titration), 64%]. When it was treated with ammonia in methyl alcohol, oxamide was first formed followed by much dimethoxysuccinamide (50% by weight of the ester used; properties as above). It was evident, therefore, that the products were essentially oxalic acid and dimethoxysuccinic acid, the amount of trimethoxyglutaric acid being negligible.

The author wishes to record his thanks to Mr. J. M. Smith, M.Sc., of Armstrong College, for valuable assistance in preparing certain of the compounds required in this investigation.

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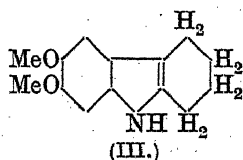
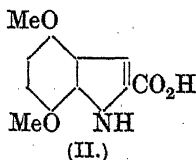
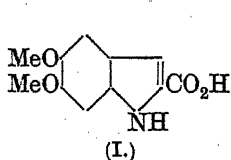
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### XLVI.—3 : 4- and 2 : 5-Dimethoxyphenylhydrazine.

By WILLIAM HENRY PERKIN, jun., and LEON RUBENSTEIN.

IN a paper published a short time since (Blaikie and Perkin, J., 1924, 125, 296; compare Kermack, Perkin, and Robinson, J., 1922, 121, 1872), the synthesis was described of several derivatives of indole containing one methoxyl group in the benzene nucleus.

The present investigation was planned as a continuation of that research and it was hoped that it might be found possible to synthesise dimethoxy-derivatives of indole and to convert these into carboline and indole-diazines related to harmine and harmaline. We also desired to prepare and study more particularly such dimethoxy-derivatives of indole and tetrahydrocarbazole as



and to compare their reactions with those of brucine with the object of obtaining further evidence bearing on the question of the positions of the methoxy-groups in that alkaloid (compare Lions, Perkin, and Robinson, J., 1925, 127, 1159). Unfortunately, the preparation of phenylhydrazines of the type  $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$  required for these experiments, from the corresponding anilines, proved to be a matter of unusual difficulty, and it is probably for this reason, and

because they are so unstable when they have been obtained, that there is no mention of these important substances in the literature. These hydrazines, and especially the 2:5-dimethoxy-derivative, do not yield satisfactory condensation products with ketones such as cyclohexanone or  $\alpha$ -ketoglutaric acid and moreover the conversion of these hydrazones into the corresponding derivatives of indole or tetrahydrocarbazole by means of the usual acid reagents, alcoholic hydrochloric or sulphuric acid, glacial acetic acid, etc., is accompanied by the formation of so much tar that the preparation of these derivatives in any quantity was found to be impossible. Other methods must therefore be sought for the synthesis of these substances, and the present communication is confined to a brief description of the dimethoxyphenylhydrazines which have been prepared and of some indole and tetrahydrocarbazole derivatives which we have succeeded in obtaining in small quantities.

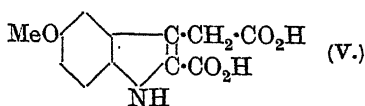
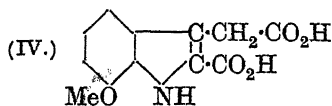
When 3:4-dimethoxyaniline hydrochloride (Fargher, J., 1920, 117, 869) dissolved in acetic acid is treated with methyl nitrite, it yields brown needles of 3:4-dimethoxybenzenediazonium chloride, and this is converted by ammonium sulphite and ammonia into red crystals of ammonium 3:4-dimethoxydiazobenzenesulphonate. This salt is readily reduced by zinc dust to ammonium 3:4-dimethoxyphenylhydrazinosulphonate, the nearly colourless needles of which rapidly decompose on exposure and yield 3:4-dimethoxyphenylhydrazine (m. p. 81°) on treatment with sodium acetate. This very unstable substance combines with cyclohexanone, and the syrupy hydrazone gives with alcoholic hydrochloric acid a small yield of 6:7-dimethoxy-1:2:3:4-tetrahydrocarbazole (III; m. p. 98°).

In a second series of experiments, 3:4-dimethoxyphenylhydrazine was condensed with ethyl pyruvate, and the syrupy hydrazone gave, with alcoholic hydrochloric acid, so small a yield of 5:6-dimethoxyindole-2-carboxylic ester (m. p. 172°; compare I) that the substance could not be further investigated. We next prepared 2:5-dimethoxyphenylhydrazine hydrochloride from 2:5-dimethoxyaniline hydrochloride (Mühlhausen, *Annalen*, 1881, 207, 254) by a process similar to that just described in the case of the 3:4-derivative, and, on treatment with sodium acetate, this yielded 2:5-dimethoxyphenylhydrazine (m. p. 85°). Both the hydrochloride and the free base are, however, so unstable and condense with ketones with such difficulty that the investigation could not be continued.

Included in this communication is a brief account of 2-carboxy-7-methoxyindole-3-acetic acid (IV) and 2-carboxy-5-methoxyindole-3-acetic acid (V) obtained respectively by condensing *o*-methoxyphenylhydrazine and *p*-methoxyphenylhydrazine with  $\alpha$ -ketoglutaric



acid and treating the products with alcoholic hydrochloric or sulphuric acid.



On testing the various methoxy-derivatives described in this communication for the brucine reaction—the orange to red coloration produced on adding a drop of nitric acid to the solution of a trace of brucine in glacial acetic acid—it was found that the monomethoxyindole derivatives give only a yellow coloration. On the other hand, 6 : 7-dimethoxytetrahydrocarbazole (III) gives an immediate pink coloration which becomes deep red on warming and, in the case of 5 : 6-dimethoxyindole-2-carboxylic ester, the yellow colour produced at first becomes wine-red on warming. The behaviour of these substances seems to support the view of Lions, Perkin, and Robinson (*loc. cit.*, p. 1161) that brucine contains the two methoxyl groups in the *o*-position to each other.

#### EXPERIMENTAL.

3 : 4-Dimethoxyphenylhydrazine,  $(\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{NH}_2$ .—Finely powdered 3 : 4-dimethoxyaniline hydrochloride (20 g.; compare Fargher, *loc. cit.*) is added to glacial acetic acid (90 c.c.), and dried methyl nitrite passed into the well-stirred mixture, the temperature being maintained between  $10^\circ$  and  $15^\circ$ . The deep brown solution is poured into dry ether (500 c.c.), and the 3 : 4-dimethoxybenzenediazonium chloride thus precipitated in brown needles is immediately dissolved in ice-water and the solution added drop by drop and at  $0^\circ$  to a well-stirred, saturated ammonium sulphite solution (60 c.c.) containing ammonia (45 c.c.;  $d$  0.880). The deep red product is kept for a few hours, and the red crystals (14 g.) of ammonium 3 : 4-dimethoxydiazobenzenesulphonate are collected (Found: N, 15.7; S, 12.0.  $\text{C}_8\text{H}_{13}\text{O}_5\text{N}_3\text{S}$  requires N, 16.0; S, 12.1%). This substance is mixed with glacial acetic acid (10 c.c.), and zinc dust (3.7 g.) gradually added, the temperature being kept between  $45^\circ$  and  $50^\circ$ . The pale brown mixture is diluted with water, the zinc precipitated as sulphide and removed by filtration in an atmosphere of hydrogen sulphide to prevent oxidation. The yellow solution is concentrated by distillation under reduced pressure; ammonium 3 : 4-dimethoxyphenylhydrazinosulphonate (9.5 g.) then separates in greyish-white crystals with a metallic lustre (Found: N, 15.7; S, 12.0.  $\text{C}_8\text{H}_{15}\text{O}_5\text{N}_3\text{S}$  requires N, 15.6; S, 12.1%).

This salt (12 g.) is boiled under reflux with alcoholic hydrochloric

acid (30 c.c. of 15%) for  $\frac{1}{2}$  hour. The mixture of 3:4-dimethoxyphenylhydrazine hydrochloride and ammonium chloride which separates from the deep red solution is collected, extracted with boiling alcohol, and filtered off; the filtrate deposits the hydrazine hydrochloride (4.5 g.) in grey prisms which, after recrystallisation from alcohol, melt at  $162^{\circ}$  (decomp.) (Found: N, 13.7.  $C_8H_{13}O_2N_2Cl$  requires N, 13.7%). 3:4-Dimethoxyphenylhydrazine hydrochloride has a strong odour of the phenylhydrazine and must be rapidly dried on porous porcelain over sulphuric acid, since it readily decomposes in contact with air, becoming a dark mass. It gradually loses hydrogen chloride under reduced pressure and the crystals dissolve in water or alcohol to solutions which rapidly become red.

3:4-Dimethoxyphenylhydrazine separates, on the addition of sodium acetate to the aqueous solution of the hydrochloride, in colourless needles, m. p.  $81^{\circ}$ , which rapidly decompose in contact with air.

6:7-Dimethoxytetrahydrocarbazole (III).—3:4-Dimethoxyphenylhydrazine hydrochloride (2.5 g.) is added to alcohol (15 c.c.) containing cyclohexanone (1.2 g.) and sodium acetate (1.4 g.). The mixture is boiled under reflux during 2 hours and poured into water; the hydrazone then separates as a syrup which does not solidify on standing or cooling. This syrup is washed with water, boiled with alcoholic hydrochloric acid (12 c.c. of 20%) for a few minutes, and the dark solution poured into water; the 6:7-dimethoxytetrahydrocarbazole that separates crystallises from dilute alcohol in pale yellow prisms, m. p.  $98^{\circ}$  (Found: C, 72.5; H, 7.6; N, 6.3.  $C_{14}H_{17}O_2N$  requires C, 72.7; H, 7.4; N, 6.1%).

Ethyl 5:6-Dimethoxyindole-2-carboxylate (compare I).—3:4-Dimethoxyphenylhydrazine hydrochloride (2.5 g.) was added to a solution of ethyl pyruvate (1.2 g.) and finely powdered sodium acetate (1.3 g.) in alcohol (25 c.c.). After boiling for 2 hours, the red solution was diluted with water; the oily hydrazone that separated did not solidify on cooling. It was washed with water and boiled for a few minutes with alcoholic hydrochloric acid (10 c.c. of 20%); on adding water, ethyl 5:6-dimethoxyindole-2-carboxylate separated in a very crude condition. This was ultimately obtained pure, crystallising from alcohol in yellow prisms, m. p.  $172^{\circ}$  (Found: C, 62.5; H, 6.0; N, 5.7.  $C_{13}H_{15}O_4N$  requires C, 62.7; H, 6.0; N, 5.7%), but the amount available did not allow of the preparation of the acid in a pure state.

2:5-Dimethoxyphenylhydrazine.—The diazotisation of 2:5-dimethoxyaniline in dilute aqueous hydrochloric acid was not feasible owing to the effervescence which accompanies the reaction even at low temperatures. Finely divided 2:5-dimethoxyaniline hydro-

chloride (20 g.; compare Mülhausen, *loc. cit.*) is added to glacial acetic acid, and dry methyl nitrite passed into the well-stirred mixture at 10°. The deep brown solution is gradually poured into dry alcohol-free ether with stirring; 2 : 5-dimethoxybenzenediazonium chloride is then precipitated in small, yellow needles and is very unstable. The ether is decanted, the crystals are rapidly washed with ether and dissolved in ice-cold water (60 c.c.), and the solution is added drop by drop to a well-cooled saturated solution of ammonium sulphite (60 c.c.) containing ammonia (40 c.c.; *d* 0.880). After remaining for a few hours, the deep red mixture is filtered, when *ammonium 2 : 5-dimethoxydiazobenzenesulphonate* remains as brick-red crystals. This substance may be crystallised from a little water, in which it is rather readily soluble (Found : N, 15.7; S, 12.1.  $C_8H_{13}O_5N_3S$  requires N, 16.0; S, 12.1%). This sulphonate (26 g.) was mixed with glacial acetic acid (23 c.c.) and water (7 c.c.), and zinc dust (7.5 g.) added at 40–50°, a little at a time. The solution, which gradually became lighter in colour, was kept at 50° for an hour, diluted with water, the zinc removed as sulphide in an atmosphere of hydrogen sulphide, and the filtrate concentrated under reduced pressure; the *ammonium 2 : 5-dimethoxyphenylhydrazinosulphonate* (19 g.) that separated as a grey, crystalline solid was recrystallised from hot alcohol (Found : N, 15.6; S, 12.1.  $C_8H_{13}O_5N_3S$  requires N, 15.6; S, 12.1%).

When this sulphonate (25 g.) was boiled under reflux with alcoholic hydrochloric acid (60 c.c. of 15%), a precipitate consisting of *2 : 5-dimethoxyphenylhydrazine hydrochloride* and ammonium chloride separated from the deep purple solution. After a few minutes, the hydrolysis was complete, more alcohol was then added and some animal charcoal, the boiling liquid filtered and concentrated; the hydrazine hydrochloride was then obtained in colourless crystals (9.5 g.) which darken above 250° (Found : C, 48.2; H, 6.0; N, 13.8.  $C_8H_{13}O_2N_2Cl$  requires C, 48.0; H, 5.9; N, 13.7%). This hydrochloride is very soluble in water and moderately soluble in alcohol and rapidly decomposes on exposure to air. *2 : 5-Dimethoxyphenylhydrazine* separated in needles on the addition of sodium acetate to the aqueous solution of the hydrochloride; after drying on porous porcelain over sulphuric acid, it melted at 84°.

*2-Carboxy-7-methoxyindole-3-acetic Acid* (IV).— $\alpha$ -Ketoglutaric acid (25 g.; compare Blaise and Gault, *Compt. rend.*, 1908, 147, 199) was dissolved in water (200 c.c.) containing sodium acetate (12 g.) and glacial acetic acid (10 c.c.), and *o*-methoxyphenylhydrazine hydrochloride (25 g.; Blaikie and Perkin, *J.*, 1924, 125, 315) in water (100 c.c.) then added. After the turbid solution had been

kept for a few hours, the yellow methoxyphenylhydrazone of  $\alpha$ -ketoglutaric acid (35 g.) was collected. It separated from benzene in yellow prisms, m. p.  $168^{\circ}$  (decomp.).

This hydrazone (15 g.) was boiled under reflux with alcoholic hydrochloric acid (25 c.c. of 15%) for  $\frac{1}{2}$  hour. The hot, very dark coloured solution was filtered from the ammonium chloride, and the filtrate kept for several hours, crystallisation being assisted by occasional scratching. The crystals were collected, washed with small quantities of alcohol, and recrystallised three times from alcohol, from which *ethyl 2-carbethoxy-7-methoxyindole-3-acetate* separated in grey needles, m. p.  $106^{\circ}$ , b. p.  $245-255^{\circ}/11$  mm. with slight decomposition (Found: C, 63.1; H, 6.0; N, 4.8.  $C_{16}H_{19}O_5N$  requires C, 62.9; H, 6.2; N, 4.6%). This ester was boiled with 10% aqueous sodium hydroxide for 2 hours and the filtered solution acidified; the *2-carboxy-7-methoxyindole-3-acetic acid* that separated crystallised from alcohol in brown needles, m. p.  $253^{\circ}$  (decomp.) (Found by titration: equiv., 251. Calc. for a dibasic acid  $C_{12}H_{11}O_5N$ : equiv., 249).

*2-Carboxy-5-methoxyindole-3-acetic Acid* (V).—*p*-Methoxyphenylhydrazine (Blaikie and Perkin, *loc. cit.*; 9.6 g.), dissolved in water (20 c.c.) containing potassium acetate (6 g.), was boiled under reflux for 2 hours with a solution of  $\alpha$ -ketoglutaric acid (8 g.) in a mixture of alcohol (30 c.c.) and water (5 c.c.). The product was filtered off and the alcohol evaporated; the *p*-methoxyphenylhydrazone of  $\alpha$ -ketoglutaric acid then remained as an oil which did not solidify on cooling and rubbing. The oil was boiled under reflux with alcoholic sulphuric acid (25 c.c. of 20%), mixed with water and ether, the tar which had separated removed by filtration, and the ethereal solution washed with water, dried, and evaporated. Since the syrupy ester did not crystallise, it was boiled under reflux with sodium hydroxide (10%) for an hour, cooled, and acidified; a gum then separated which gradually hardened and after repeated recrystallisation from alcohol, *2-carboxy-5-methoxyindole-3-acetic acid* was obtained in pale yellow needles, m. p.  $265^{\circ}$  (Found: N, 5.9; equiv. by titration, 250.  $C_{12}H_{11}O_5N$  requires N, 5.7%; equiv., 249).

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# XLVII.—*The System Ferrous Oxide-Phosphoric Acid-Water and Some of its Oxidation Products.*

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IN addition to the promised work (J., 1923, 123, 2223) on the ferrous phosphates, this paper describes a study of the oxidation of some of the ferrous-phase complexes, which has thrown fresh light on the composition of the neutral ferric phosphates.

The following ferrous phosphates are described in the literature:  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , or  $3\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , occurs in nature as *vivianite* and has been prepared by Becquerel (*Ann. Chim. Phys.*, 1833, 54, 149), Debray (*ibid.*, 1861, 61, 437), Horsford (*Sitzungsber. Akad. Wiss. Wien*, 1873, 67, 466), and Evans (*Pharm. J.*, 1897, 4, 141).  $\text{Fe}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ , or  $3\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$ , has been obtained by Gautier (*Compt. rend.*, 1893, 116, 1491). Two acid phosphates are described, viz.,  $\text{FeHPO}_4 \cdot \text{H}_2\text{O}$ , or  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , by Debray (*loc. cit.*), and  $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , or  $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , by Erlenmeyer (*Annalen*, 1878, 194, 176). Kunz-Krause (*Ber. Deut. pharm. Ges.*, 1923, 33, 20) describes a substance, containing ferrous and ferric iron and phosphoric acid, which is found in certain arable soils. This he assumes to be a basic ferrous ferric phosphate.

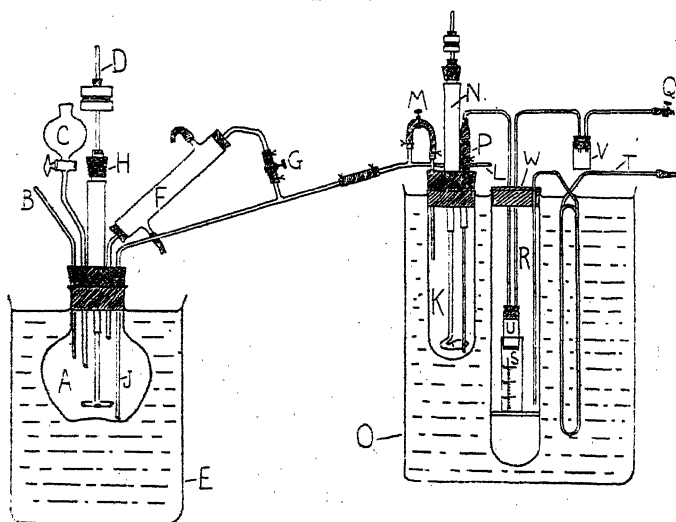
## EXPERIMENTAL.

As in the case of the ferric phosphates (*loc. cit.*), the system was studied at 70°. The equilibrium mixtures were prepared by dissolving excess of Swedish iron wire (99.75% Fe) in solutions of phosphoric acid, obtained from the same source as that used in the ferric phosphate investigation. This operation, the subsequent stirring to attain equilibrium, and the collection of the liquid and solid phases were performed in an atmosphere of carbon dioxide in an apparatus (Fig. 1) in which the rubber stoppers were coated with paraffin wax or collodion and the connexions were made with thick-walled pressure tubing carefully wired on. The iron wire, in lengths of about  $\frac{1}{2}$  inch, was placed in the flask A, and the air in the apparatus was then displaced by passing carbon dioxide, admitted through the tube B, for about 2 hours, care being taken to clear all "pockets" such as stirrer bearings. The carbon dioxide was obtained from ordinary commercial cylinders and in some cases was sufficiently pure to be used directly, but in others the gas was passed through chromous chloride solution to remove the small quantity of oxygen present, then through sodium bicarbonate solution to remove hydrochloric acid, and finally

through strong sulphuric acid. (One sample of chromous chloride solution of about 250—300 c.c. was required for a series of experiments lasting several months and during this time no alteration in the characteristic blue colour of the solution was observed. We attribute this to the fact that the solution was kept in contact with amalgamated zinc, which appears effectively to regenerate the chromous chloride after it has been oxidised, hydrochloric acid, presumably, being formed.)

Phosphoric acid solution of the required strength, freshly boiled and still hot, was run into the flask through the tap-funnel C. The mixture was then stirred with the mercury-sealed stirrer, D,

FIG. 1.



until sufficient solid phase had formed, the flask being meanwhile maintained at approximately  $70^{\circ}$  by means of the water-bath, E, and undue evaporation of water prevented by the condenser, F. The stirrer was then stopped and its bearing sealed by the rubber stopper, H, to withstand pressure. By closing the clip, G, and admitting more carbon dioxide to the flask, a portion of the mixture was forced up the tube J and into the solubility tube, K, which was one of a series of four, the remainder (not shown) being connected, in a manner similar to K, to an extension of the tube L. By suitable adjustment of screw clips (*e.g.*, M) the mixture could be admitted to one or other of these solubility tubes, the displaced carbon dioxide escaping through the mercury seals, N, etc. The tubes were supported in the thermostat, O, fitted with a glass window and maintained at  $70^{\circ} \pm 0.1^{\circ}$  by an ordinary gas-regulator.

A suitable quantity of mixture having been transferred to K, the composition of the remainder in A was altered by the addition of a few c.c. of either water or syrupy acid and the next solubility tube was filled, and so on. Four mixtures of slightly different compositions were thus obtained from one sample of iron. The object in not dissolving the iron directly in the solubility tubes was to avoid the excessive frothing which occurred when this was attempted. The flask A was of such a shape and size that the froth could not rise: further the method ensured that the mixtures were free from undissolved iron which might have interfered with the collection of phase samples and would probably have rendered the attainment of equilibrium slow and uncertain.

The mixtures were stirred for at least a week, usually longer, and from the regularity of the results it is inferred that equilibrium had then been attained. In deciding the time allowed for stirring we had to be guided by our experience of the ferric system, since it would have been impracticable, on account of the risk of oxidation, to open the solubility tubes for the purpose of withdrawing samples for trial analyses. During the stirring the pressure of the carbon dioxide in the apparatus was maintained slightly above atmospheric in order to minimise the effect of leaks (great care, however, was taken to exclude these) and diffusion through the rubber connexions, and to counterbalance any reduction in pressure due to cooling caused by a fall in level of the thermostat water.

The apparatus for collecting the phase samples was essentially the same as that used in collecting the moist solid phase in the ferric system (*loc. cit.*), with the addition of arrangements for maintaining an atmosphere of carbon dioxide in and around the filter. The figure shows it connected to the solubility tube by means of the collecting tube P, which normally was closed with a piece of glass rod. Before this connexion was made, the collecting apparatus was cleared of air by a current of carbon dioxide admitted at Q, and the jacket, R, containing the weighing-bottle, S, was also cleared, by gas entering through the tube, T, the coiled portion of which, immersed in the thermostat, served to heat the gas and thus prevent cooling of the jacket. Connexion was then made as quickly as possible, the final arrangement being shown in the figure. By suitable adjustment of the gas pressure in different parts of the apparatus the mixture of liquid and solid phases was then blown over into the weighed filter, U (any overflow being caught in the trap, V), and was filtered. The liquid phase was caught in the weighing-bottle, S. During filtration an atmosphere of carbon dioxide was maintained in R by means of T, entry of air being minimised by the loose-fitting cork cover, W.

The liquid and moist solid phases were analysed by the methods used in the ferric system. In calculating the percentage of ferrous oxide, it was assumed that the whole of the iron was present in this state, although actually it was always found that the mixtures were oxidised to some extent, usually less than 1%. This point is discussed in the following section.

Analyses of the solid phases in the dry state were also made. The drying was accomplished in some cases by washing with dry ether alone, in an atmosphere of carbon dioxide. The apparatus used consisted of a filter flask in the neck of which a wide straight adapter and a tube for admitting carbon dioxide were supported by means of a rubber stopper. The side tube of the flask carried a mercury bubbler. A filter was made up in the adapter by means of two porcelain filter plates with a layer of asbestos between them, and the neck of the adapter was fitted with a rubber stopper carrying a tube for admitting carbon dioxide, a dropping-funnel, and a capillary tube which could be closed by a screw clip fitted to a rubber extension. The air was removed from the filter flask by means of carbon dioxide and with a steady stream of this passing through the filter, the moist solid was rapidly transferred to the adapter, the stopper carrying the dropping-funnel, etc., being removed as long as was necessary to accomplish this. The air was then quickly blown out of the adapter by carbon dioxide, the capillary tube serving as outlet. This was then closed and by increasing the pressure of the carbon dioxide as much liquid as possible was expressed from the moist solid. By alternately releasing and raising the pressure by operating the clip on the capillary tube, ether could be admitted from the dropping-funnel and forced through the solid.

In cases where ether could not readily be made to pass through the solid the following procedure was adopted. The solid was shaken for a few moments in a large weighing-bottle with water, containing two or three drops of concentrated hydrochloric acid (to remove any crust of ferric salt), which was then decanted and the process repeated with two or three washings of water, alcohol, and dry ether, respectively. The solid was finally dried in a stream of carbon dioxide.

#### *Results.*

The results are in Table I and are plotted by the triangular method in Fig. 2. Analyses of the dry solids are in Table II. In the second column of Table I figures are given for the percentage of iron present in the ferric state in some of the mixtures. This was determined by rapidly dissolving the contents of the overflow trap V (Fig. I) in water acidified with hydrochloric acid and



TABLE I.

Mixture.	% oxid-ation.	Liquid phase.			Moist solid phase.		Solid phase.
		$d_{4}^{25-20^{\circ}}$	% FeO.	% $P_2O_5$ .	% FeO.	% $P_2O_5$ .	
1	1.2	1.08	2.76	7.38	—	—	2FeO, $P_2O_5$ , 5H <sub>2</sub> O.
2	—	1.16	4.38	12.06	34.9	35.51	
3	—	1.22	5.53	14.46	10.5	17.84	
4	1.6	1.20	5.48	14.96	35.9	36.0	
5	5.1	1.24	5.54	15.1	17.9	24.1	
6	—	1.31	7.71	21.6	—	—	2FeO, $P_2O_5$ , 3H <sub>2</sub> O. Well-formed crystals, average length 0.1 mm.
7	0.84	1.39	9.18	25.65	—	—	
8	—	1.43	9.88	28.25	—	—	
9	—	1.53	10.99	32.78	—	—	
10	—	1.60	11.25	37.20	19.8	38.07	
11	—	1.60	11.29	37.21	21.3	39.13	2FeO, $P_2O_5$ , 3H <sub>2</sub> O. Amorphous particles, average length 0.014 mm.
12	—	—	9.12	24.29	24.3	32.17	
13	—	1.42	10.1	27.20	21.9	32.47	
14	—	1.44	10.6	29.05	23.6	34.01	
15	0.87	1.45	10.6	29.46	23.2	33.39	
16	0.62	1.54	11.3	32.87	20.7	34.61	FeO, $P_2O_5$ , 4H <sub>2</sub> O.
17	0.92	1.55	11.5	33.99	26.3	37.81	
18	—	—	11.8	35.43	13.8	35.81	
19	2.75	1.60	11.9	36.99	—	—	
20	0.7	1.58	10.5	38.86	17.8	44.63	
21	—	1.60	8.77	41.52	18.8	46.84	FeO, $P_2O_5$ , 4H <sub>2</sub> O.
22	—	—	7.38	42.88	—	—	
23	—	1.61	6.29	46.61	16.2	48.10	
24	—	1.63	4.87	50.49	12.7	50.38	
25	—	1.63	4.01	52.02	18.2	50.52	
26	4—6	1.71	3.15	57.51	15.2	53.12	

TABLE II.

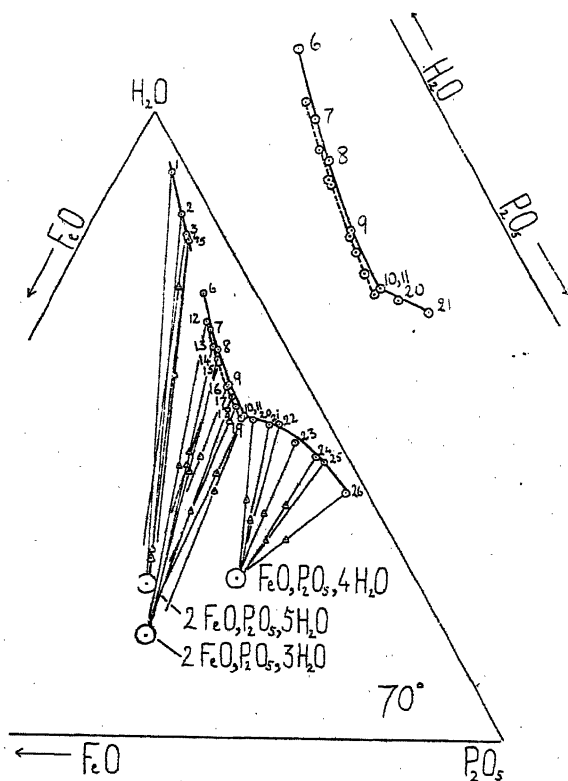
## Analysis of Dry Solid Phases.

Mixture.	Found.		Formula assigned.	Theoretical composition.	
	% FeO.	% $P_2O_5$ .		% FeO.	% $P_2O_5$ .
Specially prepared	38.0	37.8 38.0	2FeO, $P_2O_5$ , 5H <sub>2</sub> O	38.3	37.8
9	41.6	41.7 40.7	2FeO, $P_2O_5$ , 3H <sub>2</sub> O	42.4	41.8
22	24.8	49.5 49.7	FeO, $P_2O_5$ , 4H <sub>2</sub> O	25.2	49.65

titrating a portion of the solution with potassium dichromate directly and then titrating another equal portion, after reduction by stannous chloride. The method gave only a very approximate value, since the first stages of oxidation are probably confined to the liquid phase (in the four-component system FeO-Fe<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O the ferrous salts must have some region of existence as solid phases in the presence of ferric iron) and the samples taken consisted of both solid and liquid phases in varying relative amounts.

Moreover, an appreciable degree of oxidation probably occurred before the first titration could be completed. The figures were useful, however, as a rough test of the inertness of the atmosphere maintained over the mixtures during stirring. The high values given by mixtures 5 and 26 were due to the use of carbon dioxide which was subsequently found to contain 1% of oxygen. As already stated, the oxidation was neglected when the ferrous oxide

FIG. 2.



percentages were being calculated, since any attempt to determine the oxidation in liquid and moist solid phases separately, and make the necessary allowances, would have increased the already great difficulties in collecting the phase samples, besides being fraught with uncertainty as to whether the results would really represent the condition before the solubility tubes were opened. As justification for our procedure we may point to the regularity with which most of the solubility points lie on smooth curves and to the evidence afforded by the conjugation lines for the composition

of the solid phases, this evidence being confirmed by analysis of the dry solids.

The third column in Table I gives the densities of the liquid phases. The values were obtained by comparing the weights of the samples with their volumes at room temperature, estimated to 0.25 c.c. by the graduations on the side of the weighing-bottle S (Fig. 1). Since the average volume of a sample was near 20 c.c., the figures are accurate to about 1 part in 80.

With regard to the solid phases, within the range of acid concentrations studied, no neutral salt such as vivianite exists. It probably has a small range of existence in the region below the point corresponding to 7.38%  $P_2O_5$  of mixture 1, but we have found it impossible to study this region on account of the increased susceptibility to oxidation which occurs as the acid concentration diminishes. Starting with the dilute-acid region, the first solid phase found,  $2FeO, P_2O_5, 5H_2O$ , or  $FeHPO_4, 2H_2O$ , has, as far as we are aware, not been described before. Its composition is confirmed by the analysis of the dry solid (Table II) and its crystalline form is shown in the photomicrograph reproduced in Fig. 3. We are indebted to Dr. Leonard Hawkes, Head of the Geology Department at Bedford College, for the following crystallographic analysis under the microscope. Biaxial; positive; axial angle  $2V_r = ca. 60-70^\circ$ ; dispersion of optical axis  $\rho > \nu$  (?); optical axial plane parallel to the length axis of the prism. Examination was rendered difficult on account of the elongated habit and consequent tendency to settle on the slide in one position only.

The next solid phase,  $2FeO, P_2O_5, 3H_2O$  or  $FeHPO_4, H_2O$ , was described by Debray (*loc. cit.*), but doubt was subsequently cast on this author's work by Erlenmeyer (*loc. cit.*). We, however, have confirmed its existence both by the graphical method and by analysis of the dry solid (Table II). The figures are not so satisfactory as the analyses of the other dry solids owing to the very small amount of material available, but they are sufficiently conclusive. We have obtained it in two distinct forms which have slightly different solubility curves. This is shown clearly in Fig. 2, where this portion of the isotherm is drawn separately on an enlarged scale. The form showing the greater solubility is very finely divided and the particles are almost destitute of crystalline form while showing a characteristic elongated shape. A specimen of those in equilibrium with mixture 16 is shown in Fig. 4. The average length of the particles in this photomicrograph, which may be taken as representative of the whole series, is estimated to be 0.014 mm. Evidence for the composition of this solid is based solely on the conjugation lines, since all efforts to dry the

solid failed, no doubt on account of its extremely fine state of division.

The form showing the lower solubility is definitely crystalline. The type of the crystals in equilibrium with mixtures 9, 10, and 11 is shown in Fig. 5. The crystals are plates having, usually, six sides. The average diameter of those in the figure, measured in the direction of greatest length, is about 0.1 mm. Evidence for the composition of this form is based chiefly on the analysis of the dried solid in equilibrium with mixture 9 (Table II), the evidence of the conjugation lines from mixtures 10 and 11, which apparently lie at an invariant point, being inconclusive.

Mixtures 6, 7, and 8 gave a crystalline solid phase which was quite unlike any of the others in appearance. Unfortunately in no case was there sufficient material for analysis. The crystals are shown in Fig. 6. From the position of the liquid-phase points on the diagram (Fig. 2) we have concluded that it is another habit of the crystalline compound  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and accordingly have included the analytical figures in that section of Table I. The average length of the crystals (Fig. 6) was about 0.1 mm.

It appeared at first that the deposition of one form or the other was fortuitous. Subsequent perusal of the experimental notes showed, however, that in those cases where a suitable mixture (*i.e.*, one having convenient proportions of solid and liquid phases) was obtained at once in the reaction flask A (Fig. 1) and was transferred immediately to the solubility tubes, the more soluble form was obtained, whereas if further additions of iron or phosphoric acid solution were necessary, or if during the dissolution of the iron the temperature was raised or lowered (as was sometimes done to break up cakes of solid formed over-night in the reaction flask, or for other practical reasons), then the less soluble crystalline form resulted. Qualitative observations have shown that the salt has a very small temperature coefficient of solubility; moreover, its solubility is not greatly altered by varying the concentration of acid (see Fig. 2). If we assume that the molecules aggregate much more rapidly than they subsequently arrange themselves to form crystals, it is clear that the form first deposited will be an irregular aggregate, *i.e.*, an amorphous or quasi-amorphous solid. Moreover, since the solubility is scarcely affected by temperature and concentration, the aggregates may remain undisturbed for a long period unless these conditions are altered considerably. The aggregated form has more free energy than the crystalline variety and will be metastable and more soluble. The theory that the difference in solubility is connected in any way with the difference in particle size (given above) may be dismissed,

since the particles were probably too large for this factor to be operative (compare Hulett, *Z. physikal. Chem.*, 1901, **37**, 385, who found differences in the solubility of particles of diameter 0.002 mm. and less) and in any case the mixtures were stirred sufficiently long (8, 10, and 33 days) for the larger particles to grow at the expense of any small enough to give an abnormal solubility.

The solid phase in the mixtures richest in acid was the compound  $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  or  $\text{Fe}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , described by Erlenmeyer (*loc. cit.*). Its composition is amply confirmed both by the conjugation lines (Fig. 2) and by analysis of the solid in equilibrium with mixture 22 (Table II). Typical crystals are shown in Figs. 7 and 8. It has a positive temperature coefficient and crystallises spontaneously within 24 hours from appropriate liquid phases which are allowed to cool to room temperature.

The colour of the liquid phases throughout the isotherm was the pale green characteristic of the ferrous ion. The solids were also pale green. The formation of complexes, which takes place in the ferric system, does not therefore appear to occur here.

#### *Oxidation of the Mixtures.*

It has already been stated that the mixtures poor in acid were particularly susceptible to oxidation. This showed itself in the formation of reddish-brown crystals which were deposited to a greater or less extent after the mixtures had been stirred for some days, and appeared to exist in stable contact with the ferrous phosphate already present. In mixture 1, the solid phase consisted almost entirely of these crystals and therefore it was obviously useless for the purpose of the ferrous isotherm to analyse the moist solid. It was, however, of interest to find out the composition of the crystals and it was fortunately found possible to separate them from admixed ferrous phosphate by the brief action of dilute hydrochloric acid. This was discovered by watching the behaviour of the mixture under the microscope, when, on adding a drop of hydrochloric acid, the ferrous phosphate dissolved almost immediately while the brown crystals appeared to be unaltered. The solid was therefore washed, by shaking with dilute hydrochloric acid for some minutes, transferred to a filter, and washed under pressure successively with a little more dilute acid, water, alcohol, and dry ether. A little of the solid, immediately dissolved in hydrochloric acid, gave only a very faint response to the test for ferrous iron. It was therefore not a ferrous-ferrous phosphate. It gave a strong ferric reaction. Analysis of the remainder gave  $\text{Fe}_2\text{O}_3$ , 42.2;  $\text{P}_2\text{O}_5$ , 37.7.  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  requires  $\text{Fe}_2\text{O}_3$ , 42.8;  $\text{P}_2\text{O}_5$ , 38.0%, and  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4.25\text{H}_2\text{O}$  requires  $\text{Fe}_2\text{O}_3$ , 42.3;

$P_2O_5$ , 37.5%. The result thus agrees very closely with the latter formula, but we consider that, failing further evidence, it is better to regard it as incompletely dried  $Fe_2O_3 \cdot P_2O_5 \cdot 4H_2O$ .

The naturally occurring strengite has this composition, and Erlenmeyer (*loc. cit.*) claims to have prepared a neutral phosphate of this composition; his analytical figures, however, are not very conclusive, as we pointed out in our earlier paper. Crystals of our compound are shown, as dark, rectangular prisms, side by side with ferrous phosphate in Figs. 3 and 6.

Since in the ferric system we had not observed a solid which resembled these brownish-red crystals in appearance, it seemed evident that they were only stable in the presence of ferrous iron and that if oxidation were completed, the solid would change. To test this point, a mixture was prepared in the region of existence of  $2FeO \cdot P_2O_5 \cdot 5H_2O$  and was stirred at  $70^\circ$  in a solubility tube, the bearing of which was not sealed by mercury. From time to time the solid phase was examined microscopically, and the liquid tested for ferrous iron. Water was added as required to make up for loss due to evaporation through the stirrer bearing. The brown ferric salt was present from the first, and after 8 days constituted the whole of the solid phase, all the greenish-white, ferrous phosphate having disappeared. The liquid phase, however, still showed a strong ferrous reaction. After a further 8 or 9 days the brown colour of the solid had given place to a pale pink shade, resembling that of the ferric phosphates encountered in our previous work. Under the microscope, the solid was seen to be very much broken but definitely crystalline, many of the crystals having a characteristic kite-like shape. These are shown in Fig. 9, where a well-formed specimen will be seen in the middle of the picture. At this stage the liquid phase still showed a fairly strong ferrous reaction. Stirring was continued for another week without any change occurring in the appearance of the solid, but the liquid phase now gave a very weak ferrous reaction. The mixture was then left unstirred for another fortnight; it was then completely oxidised. It was stirred for a few hours to ensure equilibrium and the liquid and the solid (dry) were analysed. The liquid contained a trace of  $Fe_2O_3$  and 7.09% of  $P_2O_5$ . The solubility curve of the ferric phosphates (*loc. cit.*, p. 2230) shows that the quantity of  $Fe_2O_3$  corresponding to 7.09%  $P_2O_5$  is measurable, being about 0.1%. This slight difference in solubility may, however, be attributed to the solid in that case having been amorphous, whereas here it was crystalline, and therefore we conclude that the same compound was concerned in both cases. The reason for obtaining the crystalline form by oxidation of a ferrous mixture

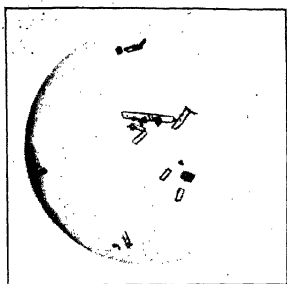


FIG. 3.— $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  and  $\beta\text{-Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  (short dark prisms).  $\times 10$ .



FIG. 4.— $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  ("amorphous")  $\times 160$ .

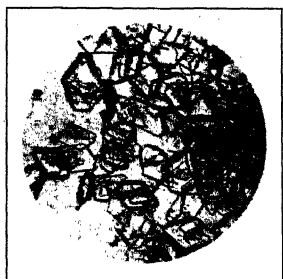


FIG. 5.— $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  (crystalline).  $\times 57$ .



FIG. 6.— $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  (crystalline) and  $\beta\text{-Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  (short dark prisms).  $\times 50$ .



FIG. 7.— $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ .  $\times 25\text{-}50$ .

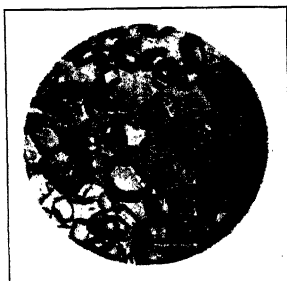


FIG. 8.— $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ .  $\times 43$ .

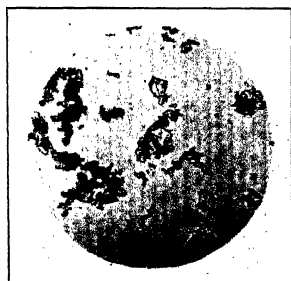


FIG. 9.— $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ .  $\times 90$

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probably lies in the gradual decrease in solubility which occurs during the process or in other factors inherent in it, which affect the velocity of crystallisation as opposed to aggregation and are evidently absent or suppressed when ferric oxide is treated with dilute phosphoric acid.

Analysis of the solid phase gave  $\text{Fe}_2\text{O}_3$ , 42.25;  $\text{P}_2\text{O}_5$ , 37.5, 37.6%, which, within the probable limits of experimental error, is the same as the composition found for the brown crystals. There are thus two neutral ferric phosphates having the composition  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  in the four-component system  $\text{Fe}_2\text{O}_3$ -FeO- $\text{P}_2\text{O}_5$ - $\text{H}_2\text{O}$  at  $70^\circ$ . We will call the pink the  $\alpha$ -form and the brown the  $\beta$ -form. Under the conditions studied, the  $\alpha$ -form is stable in the absence, or in low concentrations, of ferrous iron, whilst the  $\beta$ -form exists in the presence of medium to quite high concentrations: indeed, judging from the readiness with which it crystallises from ferrous mixtures, in spite of all efforts to maintain an inert atmosphere, it may be inferred that in this region the range of existence of solutions in equilibrium with a ferrous salt only is very limited.

The difference between the  $\alpha$ - and the  $\beta$ -salt may be explained in a similar way to that applied in the case of the neutral ferric phosphates at  $25^\circ$  (*loc. cit.*). As we mentioned there, the work of Weinland and Engraber showed that the pink ferric phosphates were probably complex ferri-phosphates. Thus we may suppose that the pink  $\alpha$ -form has the constitution  $[\text{Fe}(\text{PO}_4)_2]\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , while the brown  $\beta$ -salt is a true ferric phosphate,  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ . Support for the latter supposition is given by the colour changes which ferrous phosphate solutions undergo on oxidation: the original green colour changes to brown and finally to pink. The intermediate brown colour may well be due to the ferric ion, and it is the  $\beta$ -form which can exist at this stage.

It is now seen that we were in error in our earlier work in attributing five molecules of water to the solid phase in equilibrium with the weakly acid solution at  $70^\circ$ . That such a hydrate does exist appears to have been confirmed by Weinland and Engraber, and in our own work at  $25^\circ$  there seems to be little doubt that it was present. At  $70^\circ$ , however, the  $\alpha$ -salt with four molecules of water is stable, at least in the region in which the above oxidation experiment terminated.

#### Summary.

1. The system  $\text{FeO}$ - $\text{P}_2\text{O}_5$ - $\text{H}_2\text{O}$  has been studied at  $70^\circ$ , between the concentrations 7.38 and 57.51%  $\text{P}_2\text{O}_5$ . Within this range the stable solid phases are the acid salts  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ,  $2\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ , and  $\text{FeO} \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , the first of which has, as far as is known, not been described before.

2. By the oxidation of phases poor in acid, two neutral ferric phosphates, both having the composition  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , are deposited. The brown  $\beta$ -form exists in contact with liquid phases having high to medium concentrations of ferrous iron; at lower concentrations, the pink  $\alpha$ -form becomes stable.

The authors wish to express their indebtedness to Dr. J. F. Spencer for much helpful advice and to Mr. A. Watson for carrying out many of the analyses.

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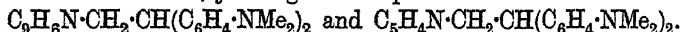
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## XLVIII.—Condensations involving Reactive Methyl Groups in Heterocyclic Bases.

By JAMES ERNEST HUMPHRIES.

THE reactions described below, *viz.*, the condensation of quinaldine, *p*-toluquinaldine, and  $\alpha$ -picoline and of their quaternary salts with Michler's hydrol and a nitrosoamine, are further examples of the reactivity of methyl and methylene groups towards the groups  $\text{:C:O}$  and  $\text{:N:O}$ . Fosse (*Ann. Chim. Phys.*, 1906, 8, 18) found that, in presence of acetic acid as condensing agent, Michler's hydrol (4:4'-tetramethyldiaminobenzhydrol) reacted with the methylene group of such compounds as acetoacetic ester, acetylacetone, etc. Quinaldine and  $\alpha$ -picoline condense readily with the hydrol under the same conditions, yielding the compounds



The condensations can also be effected by zinc chloride. The methiodides of the heterocyclic bases react more readily than the bases themselves and under conditions in which the latter are not affected, *viz.*, in alcoholic solution. The condensation products are similar to the *leuco*-compounds of the triphenylmethane dyes and are readily oxidised by lead peroxide and acetic acid to red dyes.

The quaternary salts do not react with benzenediazonium sulphate, but condense readily with *p*-nitrophenylnitrosoamine, in cold alcoholic solution. The resulting compounds were phenylhydrazones, *e.g.*,  $\text{C}_9\text{H}_6\text{N}(\text{MeI}) \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ . This reaction differs from that of Adams (*Chem. Zentr.*, 1923, 94, I, 1591), who added simultaneously solutions of potassium hydroxide and diazotised aniline to an aqueous solution of quinaldine methiodide and obtained the azo-compound,  $\text{C}_9\text{H}_6\text{N} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_5$ .

The bases themselves and their hydrochlorides do not react with

the nitrosoamine, so that in both reactions the reactivity of the  $\alpha$ -methyl group is enhanced by converting the tertiary base into a quaternary compound.

#### EXPERIMENTAL.

*Condensations with Michler's Hydrol.*—(1) *Quinaldine*. A solution of equimolecular quantities of the hydrol and quinaldine in glacial acetic acid was warmed on a water-bath until the intense blue colour changed to deep red (1 hour). Ammonium hydroxide then precipitated a dark green oil which, isolated by means of ether, was obtained in pale-yellow needles, m. p.  $131^\circ$  (Found: N, 10.7.  $C_{27}H_{29}N_3$  requires N, 10.6%).

The condensation product (1 mol.) was dissolved in hydrochloric acid (3 mols.) and enough water to make a 2% solution; acetic acid (2 mols.) was added and the whole cooled to  $0^\circ$ . Then, with rapid stirring, freshly prepared lead peroxide (1 mol.) was quickly added. The solution became intensely red. The lead was removed as sulphate, and the oxidation product obtained by addition of sodium hydroxide and extraction with chloroform. A red, amorphous powder was precipitated from the dried chloroform extract on adding ether. The *oxalate* was analysed (Found: N, 8.0.  $C_{30}H_{32}O_6N_3$  requires N, 7.95%).

The oxidation product dyes silk violet. Its salts are red, but the pseudo-base,  $C_9H_6N \cdot CH : C(C_6H_4 \cdot NMe_2)_2$ , is brown.

(2) *p-Toluquinaldine*. The condensation product (m. p.  $152^\circ$ ) was similar to that formed from quinaldine (Found: N, 10.1.  $C_{28}H_{31}N_3$  requires N, 10.3%).

(3)  $\alpha$ -*Picoline*. The condensation was carried out as in (1) and pale yellow crystals, m. p.  $187^\circ$ , were obtained (Found: N, 12.1.  $C_{23}H_{27}N_3$  requires N, 12.2%).

(4) *p-Toluquinaldine methiodide*. The condensation, which also proceeds in glacial acetic acid, was effected by boiling an alcoholic solution of the reactants for a few minutes. On concentrating the solution, copper-red needles, m. p.  $160^\circ$  (decomp.), were obtained (Found: I, 23.2; N, 7.6.  $C_{29}H_{34}N_3I$  requires I, 23.05; N, 7.6%).

The corresponding methochloride, obtained by condensing *p*-toluquinaldine methochloride and the hydrol, was oxidised as in (1), but the deep-red, amorphous dye which was formed could not be obtained pure.

*Condensations with p-Nitrophenylnitrosoamine.*—When equal molecular quantities of benzenediazonium sulphate and *p*-toluquinaldine methiodide were mixed in alcoholic solution at the ordinary temperature, the solution turned red and golden-yellow plates, m. p.  $133^\circ$ , of the *periodide* of *p*-toluquinaldine methiodide

immediately began to separate (Found: N, 2.55; I, 69.1.  $C_{12}H_{14}NI_3$  requires N, 2.5; I, 68.9%). This was readily reduced to the methiodide by sulphur dioxide or stannous chloride, and was also formed by warming the methiodide and iodine in glacial acetic acid.

No condensation took place when the methiodide was replaced by the methonitrate of *p*-toluquinaldine.

(1) *p*-Toluquinaldine methiodide. The nitrosoamine was prepared by Schraube and Schmidt's method (*Ber.*, 1894, 27, 514). Equimolecular quantities of the nitrosoamine and the methiodide, each in alcoholic solution, were mixed at 0°. The crystalline precipitate was recrystallised from methyl alcohol, reddish-brown needles, m. p. 244°, being thus obtained (Found: N, 12.3; I, 28.6.  $C_{18}H_{19}O_2N_4I$  requires N, 12.5; I, 28.35%).

That the new compound was the *p*-nitrophenylhydrazone of 2-formyl-6-methylquinoline was proved in the following way. *p*-Toluquinaldine methiodide was condensed with *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, 45, 1738), yielding the Schiff's base,  $C_{10}H_{10}N(MeI) \cdot CH:N \cdot C_6H_4 \cdot NMe_2$ , in green needles, m. p. 207 (decomp.). This was hydrolysed by boiling with dilute hydrochloric acid, and *p*-nitrophenylhydrazine added. The hydrazone so found was identical with the product of the nitrosoamine condensation.

(2) *Quinaldine methiodide*. The product formed red needles, m. p. 250° (Found: I, 29.4.  $C_{17}H_{15}O_2N_4I$  requires I, 29.3%).

(3) *Quinaldine ethiodide* gave red needles, m. p. 262° (Found: I, 28.5.  $C_{18}H_{17}O_2N_4I$  requires I, 28.3%).

(4)  $\alpha$ -*Picoline methiodide* gave yellow needles, m. p. 260° (Found: I, 33.4.  $C_{13}H_{13}O_2N_4I$  requires I, 33.1%).

In the last three cases the identity of the product was confirmed as in the case of (1).

The author wishes to thank Dr. W. H. Mills, F.R.S., for his valued advice.

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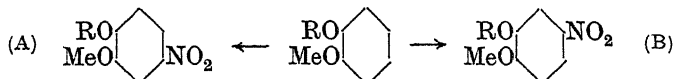
[Received, December 15th, 1925.]

## XLIX.—*The Relative Directive Powers of Groups of the Forms RO and RR'N in Aromatic Substitution. Part I.*

By JAMES ALLAN and ROBERT ROBINSON.

THE nitration of veratrole in cold acetic acid solution proceeds extremely smoothly and 4-nitroveratrole is obtained in almost theoretical yield. Careful search reveals no trace of 3-nitro-

veratrole or of 4:5-dinitroveratrole in the product. An ether of guaiacol, other than veratrole, will naturally yield two nitro-derivatives in relative amounts which depend on the ratio of the directive powers of the groups RO and MeO.



Since the meta-directing influence of the alkyloxy-group is zero, we may assume that Directive Power of OR/Directive Power of OMe = % of (A) formed in the reaction/% of (B) formed in the reaction. In order to obtain numbers which can be compared, the directive power of MeO is taken to be 100. In every case nitration was carried out in cold glacial acetic acid solution, and the composition of the product determined by the method of thermal analysis with the aid of data derived from mixtures of substances of the types (A) and (B), which were prepared by appropriate alkylation of 4- and 5-nitroguaiacols, respectively. The directive powers found in this way were: MeO, 100; EtO, 135; Pr<sup>n</sup>O, 128; Pr<sup>i</sup>O, 150; *n*-C<sub>4</sub>H<sub>9</sub>O, 123; CH<sub>2</sub>PhO, 113. It is interesting to note that Sonn and Patschke (*Ber.*, 1925, 58, 1698) \* have observed the order CH<sub>2</sub>·CH·CH<sub>2</sub>·O > EtO > Pr<sup>n</sup>O > MeO for the orienting influence of these groups in the course of the preparation of ethers of β-resorcyraldehyde by the Gattermann synthesis.

## EXPERIMENTAL.

*Mixtures of 4-Nitro-2-ethoxyanisole and 5-Nitro-2-ethoxyanisole.*—5-Nitroguaiacol was prepared by the method of Pollecöff and Robinson (*J.*, 1918, 113, 648) and in the nitration of 2-methoxyphenyl carbonate it was found advantageous to continue stirring at 0° for 3·5 hours. The ethylation of 5-nitroguaiacol was carried out by Ludwig's method (*Monatsh.*, 1900, 21, 100) and also by the xylene-ethyl sulphate-potassium carbonate process. The yield was 65% and the m. p. 102°. 5-Nitro-2-ethoxyanisole (Freyss, *Bull. Soc. ind. Mulhouse*, 1901, 70, 375), m. p. 85°, was similarly obtained in 60% yield from 4-nitroguaiacol. The freezing points were determined in a double-jacketed glass tube with the usual precautions. Nucleation and stirring were practised and the thermometer was graduated in fifths of a degree, but could be read accurately to the nearest 0·1°. As in all subsequent cases, the entire range of composition was examined and a portion of the curve selected for closer study either because the readings

\* The work here described was carried out in 1922—1923 and the numerical results were disclosed when Part IV of this series was read at a meeting of the Society in June, 1925 (compare *J. Soc. Chem. Ind.*, 1925, 44, 659r).

were more free from ambiguity in that region, or because the nitration mixture has a freezing point lying well inside the section.

The following data were employed in the present instance, the first number of each pair representing the percentage of 5-nitro-2-ethoxyanisole in the mixture: 31.5, 83.7°; 37.8, 79.5°; 42.4, 75.4°; 50.9, 66.3°; 54.1, 62.6°; 55.6, 60.1°.

*Nitration of 2-Ethoxyanisole.*—2-Ethoxyanisole, b. p. 213° (Tiemann and Koppe, *Ber.*, 1881, 14, 2018) (10 g.) mixed with purified acetic acid (30 g.) was nitrated by the gradual addition of nitric acid (12.5 c.c.;  $d$  1.42) in acetic acid (30 g.). The mixture was mechanically stirred and cooled in a freezing mixture; the highest temperature reached was 12°. After 45 minutes, the product crystallised and the temperature remained stationary at  $-1^\circ$ ; water was then added, the solid collected, well washed and dried (yield 95%). The product (A) was crystallised from methyl alcohol (50 c.c.), and equilibrium ensured by keeping for 5 hours at 16°. The pale yellow crystals were collected, thoroughly drained under pressure, and dried (10.68 g.) (B). 7.1652 G. of (B) mixed with 0.5 g. of 4-nitro-2-ethoxyanisole froze at 66.0°. Hence from the graph, (B) contains 4.82 g. of 4-nitro-2-ethoxyanisole and 5.85 g. of 5-nitro-2-ethoxyanisole. In order to determine the composition of (A) it is necessary to estimate the solubilities of the isomerides in methyl alcohol at 16° and in presence of each other. 4-Nitro-2-ethoxyanisole (6.1860 g.) and 5-nitro-2-ethoxyanisole (3.8571 g.) were allowed to saturate methyl alcohol (25 c.c.) at 16°. The solid residue weighed 9.13 g. and its f. p. was 81.5°, corresponding to 34.9% of 5-nitro-2-ethoxyanisole. Combining these results, it appears that (A) contains 42.5% of 4-nitro-2-ethoxyanisole and 57.5% of 5-nitro-2-ethoxyanisole. That (B) contained the two isomerides only was shown by the fact that 7.1652 g. of (B) mixed with 1.0 g. of 4-nitro-2-ethoxyanisole froze at 68.9°. This corresponds to 51.4% of 4-nitro-2-ethoxyanisole, whereas the percentage calculated from the assumed composition of (B) is 51.9. This result and similar ones recorded below also guarantee the correct location of the points on the graph corresponding to the observed freezing points. The directive power of EtO relative to MeO (100) is therefore 135 in this series.

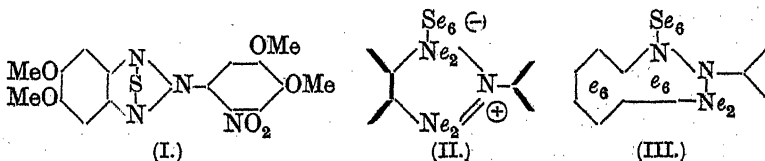
4:5-Dinitro-2-ethoxyanisole.—The mixture of mononitro-2-ethoxyanisolcs was dissolved in cold nitric acid ( $d$  1.42) and next day the product was precipitated by water and collected; it crystallised from alcohol in very pale yellow needles, m. p. 150° (yield almost quantitative) (Found: N, 11.6.  $C_9H_{10}O_6N_2$  requires N, 11.6%). The m. p. of this methoxyethoxy-compound appears anomalous, since the related dimethoxy- and diethoxy-compounds melt at

132° and 113° respectively. By successive reduction with zinc dust in aqueous alcoholic hydrochloric acid solution, addition of sodium acetate and of a solution of phenanthraquinone in aqueous sodium bisulphite, and boiling, a flocculent, yellow precipitate of 3-methoxy-2-ethoxyphenanthraphenazine is obtained. Crystallised from xylene, the substance has m. p. 231°, gives a deep magenta solution in sulphuric acid, and fluoresces violet in benzene (Found : N, 8.2.  $C_{23}H_{18}O_2N_2$  requires N, 7.9%).

6'-Nitro-3' (or 4')-methoxy-4' (or 3')-ethoxyphenyl-4 : 5-thiotriazocatechol Methyl Ethyl Ether.—Jones and Robinson (J., 1917, 111, 910) obtained a compound,  $C_{16}H_{16}O_6N_4S$ , by the action of hydrogen sulphide on 4 : 5-dinitroveratrole in aqueous alcoholic ammonia. This substance was shown to be a nitro-derivative, reducible to a related diazotisable amine, and it was considered to be 6-nitro-veratryl-4 : 5-thiotriazoveratrole (I).

We have applied the reaction under similar conditions to 4 : 5-dinitro-2-ethoxyanisole and have thus obtained a yellow compound which was crystallised by the addition of alcohol to its solution in nitrobenzene. The substance closely resembles nitroveratryl-thiotriazoveratrole and appears to be homogeneous. The yellow, rectangular plates, m. p. 175°, are sparingly soluble in alcohol or ether and moderately readily soluble in benzene or chloroform (Found : C, 51.6; H, 4.4; S, 7.8.  $C_{18}H_{20}O_6N_4S$  requires C, 51.4; H, 4.8; S, 7.6%).

In these substances the  $SN_3$  group is associated with 24 valency electrons and on the electronic theory of valency a reasonable assumption regarding the constitution of the thiotriazo-nucleus is that it contains the bipolar ion (II), where each straight line in thin type represents two electrons.



It is very probable, however, that the nucleus has aromatic character and this requires a contribution of four electrons from the  $SN_3$  group towards an aromatic sextet, two more being derived by fusion with the benzene nucleus. By analogy with glyoxaline these four electrons should be derived from the nitrogen atom joined to sulphur and from the double bond joining the other nitrogen atoms, giving the expression (III). Here, the sulphur atom is favourably situated for the purpose of increasing its covalency with the nitrogen atom and thus neutralising both its

own electrical charge and that on the ring members. The formula (II) is derived from an *o*-thionitrosoazobenzene derivative by a process of internal addition precisely analogous to that assumed by Burkhardt and Lapworth (J., 1925, 127, 1749) for the first stage of the reaction between nitrosobenzene and ethyl methylenemalonate. In the case we have discussed, the place of the unsaturated ester is taken by the thionitroso-group and the place of the nitroso-group by the azo-group.

4-Nitro-2-propoxyanisole, prismatic needles, m. p. 106° (Found : C, 56.6; H, 6.1.  $C_{10}H_{13}O_4N$  requires C, 56.9; H, 6.2%) and 5-nitro-2-propoxyanisole, hexagonal tablets, m. p. 72° (Found : C, 56.9; H, 6.5%) were obtained in 70% and 65% yield, respectively, from 5-nitroguaiacol and 4-nitroguaiacol by the action of propyl iodide and potassium hydroxide in boiling alcoholic solution during 5–6 hours.

Mixtures of 4-nitro-2-propoxyanisole and 5-nitro-2-propoxyanisole had the following freezing points, the first number of each pair representing the percentage of 4-nitro-2-propoxyanisole in the mixture : 31.5, 55.5°; 34.2, 59.9°; 36.7, 63.5°; 41.0, 69.6°; 44.2, 73.4°; 50.5, 79.3°; 53.6, 82.4°; 57.0, 84.6°.

*Nitration of 2-Propoxyanisole.*—2-Propoxyanisole (10 g.), b. p. 220–225° (Cahours, *Compt. rend.*, 1877, 84, 1195, gives 240–245°), dissolved in pure acetic acid (45 g.) was nitrated below 9° by the gradual addition with stirring of a mixture of nitric acid (15 c.c.; *d* 1.42) and acetic acid (35 g.). After one hour the product was precipitated by water, collected, washed and dried (A; 96% yield). This material was crystallised from 70 c.c. of 80% ethyl alcohol and after attaining equilibrium at 16° the solid was isolated (B) (10.79 g.). (B) froze at 75.2°, corresponding to 46.2% of 4-nitro-2-propoxyanisole. This was verified by adding 0.5213 g. of 4-nitro-2-propoxyanisole, when the f. p. was 77.6°, corresponding to 48.7% of 4-nitro-2-propoxyanisole (calc., 48.7%). A mixture of the isomerides (11.8861 g.), f. p. 78.5° (corresponding to 49.75% of 4-nitro-2-propoxyanisole) was allowed to reach equilibrium with 80% alcohol (40 c.c.) at 16°. The isolated solid froze at 80.0° (corresponding to 51.25% of 4-nitro-2-propoxyanisole) and the alcohol dissolved 0.5151 g. From these results it may be calculated that (A) contains 43.9% of 4-nitro-2-propoxyanisole and 56.1% of 5-nitro-2-propoxyanisole. The directive power of  $Pr^2O$  is, accordingly, 128.

4 : 5-Dinitro-2-propoxyanisole, obtained in theoretical yield from the mono-nitration product of 2-propoxyanisole by the action of nitric acid (*d* 1.42), crystallises from alcohol in needles, m. p. 143° (Found : C, 47.0; H, 5.0.  $C_{10}H_{12}O_6N_2$  requires C, 46.9; H, 4.7%).



4-Nitro-2-isopropoxyanisole, pale yellow, prismatic needles, m. p.  $83^{\circ}$  (Found: C, 56.7; H, 6.1.  $C_{10}H_{13}O_4N$  requires C, 56.9; H, 6.2%) and 5-nitro-2-isopropoxyanisole, yellow prisms, m. p.  $53^{\circ}$  (Found: C, 57.0; H, 6.3%), were obtained like the ethyl and propyl compounds previously described, but in this case the yields were only 30% and 15%, respectively. The freezing points of mixtures of the isomerides were the following, the first number of each pair giving the percentage of 5-nitro-2-isopropoxyanisole: 24.6,  $69.7^{\circ}$ ; 30.4,  $66.7^{\circ}$ ; 35,  $63.7^{\circ}$ ; 39.5,  $60.2^{\circ}$ ; 48.1,  $53.8^{\circ}$ .

*Nitration of 2-isopropoxyanisole.*—Guaiacol was converted into its isopropyl ether by boiling in alcoholic solution with an equivalent of potassium hydroxide and isopropyl iodide. The yield of a colourless oil, b. p.  $210-215^{\circ}$ , was 90% (Found: C, 71.6, 71.6; H, 8.4, 8.2.  $C_{10}H_{14}O_2$  requires C, 72.3; H, 8.4%). Somewhat low results in carbon estimations appear to be normal in the case of these ethers. Thus Cahours (*loc. cit.*) found C, 71.7 for 2-propoxyanisole. The nitration (of 8 g.) was carried out in the usual manner, giving a product (A) in 92% yield which was crystallised from 45 c.c. of 80% alcohol. After standing at  $15^{\circ}$ , the solids (B) were isolated (7.6978 g.). A mixture of 6.5663 g. of (B) with 2.4954 g. of 4-nitro-2-isopropoxyanisole froze at  $57.0^{\circ}$ , corresponding to 56.0% of 4-nitro-2-isopropoxyanisole. Hence (B) contains 39.3% of 4-nitro-2-isopropoxyanisole. A further 0.34 g. of 4-nitro-2-isopropoxyanisole was added and the f. p. was then  $58.2^{\circ}$ , corresponding to 57.8% (calc., 57.6%) of the 4-nitro-derivative. 60 C.c. of 80% alcohol dissolved 2.3089 g. of a mixture of 4-nitro-2-isopropoxyanisole (5.0 g.) and 5-nitro-2-isopropoxyanisole (4.641 g.) at  $15^{\circ}$  and the residue was isolated. 6.3365 G. of this product mixed with 4-nitro-2-isopropoxyanisole (1.1973 g.) had f. p.  $61.3^{\circ}$ , corresponding to 61.75% of the 4-nitro-derivative. From the above data it may be calculated that (A) contains 40.0% of 4-nitro-2-isopropoxyanisole and the directive power of  $Pr^{\beta}O$  is 150.

4:5-Dinitro-2-isopropoxyanisole, prepared from the mixture of mononitro-derivatives of 2-isopropoxyanisole in the usual manner, is much more readily soluble in alcohol than the propoxy-isomeride and crystallises in rectangular plates, m. p.  $129^{\circ}$  (Found: C, 46.8; H, 5.0.  $C_{10}H_{12}O_6N_2$  requires C, 46.9; H, 4.7%).

4-Nitro-2-n-butoxyanisole, m. p.  $74^{\circ}$  (Found: C, 58.3; H, 7.0.  $C_{11}H_{15}O_4N$  requires C, 58.7; H, 6.7%), and 5-nitro-2-n-butoxyanisole, pale yellow prisms, m. p.  $56^{\circ}$  (Found: N, 6.6.  $C_{11}H_{15}O_4N$  requires N, 6.2%), were obtained in the usual manner in 60% and 55% yield, respectively. The freezing points of mixtures of the isomerides are the following, the first number of each pair indicating the percentage of 4-nitro-2-n-butoxyanisole: 25.5,  $39.8^{\circ}$ ; 28.3,

37.5°; 33.2, 32.6°; 36.5, 30.4°; 39.6, 33.2°; 42.7, 35.3°; 45.1, 35.7°; 46.9, 35.5°; 50.7, 39.6°; 52.2, 41.8°; 53.8, 44.1°.\* A compound, f. p. 35–36°, appears to be formed containing 44% of the 4-nitro-isomeride. The eutectic on the side of the 4-nitro-isomeride is near 35° and on the side of the 5-nitro-isomeride it is near 30°.

*Nitration of 2-n-Butoxyanisole.*—The *n*-butyl ether of guaiacol was obtained in almost quantitative yield in the usual manner. It is a colourless oil, b. p. 236–239° (Found: C, 72.8; H, 8.8.  $C_{11}H_{16}O_2$  requires C, 73.3; H, 8.9%), and, on nitration in acetic acid below 12°, gave a mixture of mononitro-derivatives (A) in 96% yield. This material was dissolved in 65 c.c. of 80% alcohol and, on cooling, an oil separated and subsequently crystallised. After keeping at 16°, the product (B) was collected, well drained, and pressed, and finally dried at 95° during an hour. (B) (8.5006 g.) mixed with 4-nitro-2-*n*-butoxyanisole (0.3088 g.) froze at 37.3°, corresponding to a mixture containing 49.0% of the 4-nitro-isomeride. On adding 0.3054 g. of the 4-nitro-isomeride, the f. p. observed was 39.6°, corresponding to 50.7% of the 4-nitro-isomeride (calc., 50.7%). Further addition of 4-nitro-2-*n*-butoxyanisole (0.2977 g.) gave a mixture found to contain 52.1% of the 4-nitro-isomeride (calc., 52.2%). A mixture of 4-nitro-2-*n*-butoxyanisole (6.0833 g.) and 5-nitro-2-*n*-butoxyanisole (6.5902 g.) was crystallised from 80% alcohol (50 c.c.) and, after standing at 16°, the solid was isolated and found to weigh 11.2734 g. and to freeze at 38.5°, corresponding to 49.75% of the 4-nitro-isomeride.

From the above data it follows that (A) contains 44.8% of 4-nitro-2-*n*-butoxyanisole and 55.2% of the 5-nitro-isomeride. Consequently the directive power of *n*- $C_4H_9\cdot O$  is 123.

4:5-Dinitro-2-*n*-butoxyanisole, obtained by further nitration of the mixed mononitro-derivatives in excellent yield, crystallises from alcohol in faintly yellow needles, m. p. 97° (Found: C, 48.7; H, 4.9.  $C_{11}H_{14}O_6N_2$  requires C, 48.9; H, 5.2%).

4-Nitro-2-benzyloxyanisole was obtained in 75% yield from 5-nitroguaiacol by the action of benzyl chloride and potassium hydroxide in boiling alcoholic solution. It crystallises from alcohol in one of two forms, m. p. 93° and m. p. 98° (Found in material, m. p. 93°: C, 64.7; H, 5.2, and in material, m. p. 98°: C, 64.7; H, 5.1.  $C_{14}H_{13}O_4N$  requires C, 64.9; H, 5.0%).

5-Nitro-2-benzyloxyanisole, m. p. 82°, was similarly obtained from 4-nitroguaiacol in 55% yield (Found: C, 64.9; H, 5.0%). The

\* In this case and also that of the benzyloxy-series, sharper and more consistent readings were obtained if, after thorough nucleation, stirring ceased when the cooling became very slow in the neighbourhood of the freezing point.

freezing points of mixtures of the isomerides were the following, the first number of each pair indicating the percentage of 5-nitro-2-benzyloxyanisole: 17.1, 85.0°; 23.7, 80.0°; 33.6, 72.9°; 37.2, 69.2°; 41.3, 65.2°; 46.0, 57.2°.

*Nitration of 2-Benzyloxyanisole.*—2-Benzyloxyanisole (9.766 g.) dissolved in acetic acid (65 c.c.) was nitrated by the gradual addition of a mixture of nitric acid (20 c.c.;  $d$  1.42) and acetic acid (35 c.c.) with cooling in ice and stirring. The temperature rose momentarily to 18°, but quickly fell to 8°. After an hour, water was added and the product (A) collected, washed and dried (yield 98%). The material was crystallised from 80% alcohol (80 c.c.) at 16°, and the solid (B) completely freed from adherent mother-liquor and dried (11.1332 g.). A mixture of (B) (6.3452 g.) and 4-nitro-2-benzyloxyanisole (2.0015 g.) froze at 67.0° and therefore contained 39.5% of 5-nitro-2-benzyloxyanisole. On adding more 4-nitro-2-benzyloxyanisole (0.451 g.), the f. p. was 69.1°, corresponding to 37.3% of the 5-nitro-isomeride in the mixture (calc., 37.5%). Alcohol (50 c.c. of 80%) was saturated at 16° by the addition of 4-nitro-2-benzyloxyanisole (5.0 g.) and 4-nitro-2-benzylanisole (4.2528 g.). The solvent contained 0.3972 g. of the mixed isomerides, whilst the separated material had f. p. 59.5° and thus contained 44.8% of 5-nitro-2-benzyloxyanisole. From the above data it appears that (A) contained 53.0% of 5-nitro-2-benzyloxyanisole and 47.0% of the 4-nitro-isomeride and that the directive power of  $\text{CH}_2\text{PhO}$  is 113.

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L.—*The Relative Directive Powers of Groups of the Forms RO and RR'N in Aromatic Substitution. Part II. The Nitration of some 2-Benzyloxyanisoles substituted in the Benzyl Group.*

By ALBERT EDWARD OXFORD and ROBERT ROBINSON.

IN this communication the method described in the preceding paper is applied to the determination of the directive powers of the *m*- and *p*-nitrobenzyloxy- and *m*-methoxybenzyloxy-groups.

2-*m* (or *p*)-Nitrobenzyloxyanisole is much more difficult to

nitrate than is 2-benzyloxyanisole and it is evident that the introduction of the nitro-group has the effect of depressing the reactivity of the molecule as a whole. This effect is, however, felt to a greater relative extent by the benzyloxy-group than by the methoxyl. In Part I it is shown that the directive power of the benzyloxy-group (MeO, 100) is 113 and we now find that the *m*-nitrobenzyloxy- and *p*-nitrobenzyloxy-groups have, within the limits of experimental error, identical directive powers, namely, 67. Obviously the true value should be smaller still, because a portion of the inhibitory effect of the nitroxyl has been experienced by the methoxyl group. Since the nitro-group exerts its influence to an equal extent from the meta- and para-positions in the benzyl nucleus, it is not an alternating effect but, in all probability, a general polar effect which is under observation. The existence of general electrical effects is widely recognised, but it must be emphasised that, no less than in the case of the alternating effects, a knowledge of the mechanism of the reaction is necessary before a conclusion can be reached as to whether a particular process should be facilitated or hindered. An example will illustrate our meaning. Olivier (*Rec. trav. chim.*, 1922, 41, 646) has shown that the hydrolysis of *o*-, *m*-, and *p*-nitrobenzyl chlorides in aqueous alcohol is much slower than that of benzyl chloride or any of its chloro-, bromo-, or methyl derivatives and this is another clear case of the general electrical effect of the nitro-group. The fact that the nitrophenols and nitrobenzoic acids, compared with phenol and benzoic acid, respectively, are strong acids shows that the nitro-group increases the affinity for the negative charge, whilst the weak basic nature of the nitroanilines, compared with aniline, shows that the introduction of a nitro-group decreases the affinity for the positive charge. An important exemplification of the latter point is found in the high chemical reactivity of nitro-substituted diazonium salts. Now, under the conditions of Olivier's experiments, the most acceptable view of the mechanism of the hydrolysis is that which postulates partial or complete dissociation of the nitrobenzyl chlorides at some stage and possibly as a result of oxonium salt formation with water or alcohol. Any such process will be inhibited if the affinity of the substituted benzyl group for the positive charge is diminished. Hence, on this mechanism, the theory of the general electrical effect of the nitro-group requires that the hydrolysis of a nitrobenzyl chloride should be slower than that of benzyl chloride. If, however, the benzyl chlorides were hydrolysed through the intermediate formation of a complex anion which subsequently recovered neutrality by ejecting chloridion, then the nitro-group, by increasing the affinity for the negative charge, would

facilitate the process.\* Conversely, the introduction of nitro-groups into a molecule should retard the formation of complex kations such as those resulting from the attack of an aromatic compound by a diazonium ion, and this is in accordance with experience. It is a short step to the general case of aromatic substitution in which the nucleus is attacked by the positive end of a polarised complex rather than by a positive ion, and the same principles apply. If an aromatic nucleus, A, reacts with a complex,  $\oplus B-C\ominus$ , then the charge on B is transferred to the nucleus and the bipolar ion,  $\oplus A-B-C\ominus$ , is produced. Circumstances, such as the introduction of nitroxyl, which reduce the affinity of A for the positive charge must retard the process. In our experiments, the nitro-groups gave rise to no alternating effect whatever, but it should be noted that the system is a complex one summarised as : modifying group—activating centre—point of reaction. That is, the effect of the nitro-groups on the reacting nucleus is only experienced through an oxygen atom, which must be regarded as the effective key-atom. In Olivier's experiments very weak alternating effect (in the expected sense) is superposed on the powerful general effect, whilst Harrison (private communication) has shown that the hydration of 3 : 4'-dinitrotolane yields nothing but 3-nitrophenyl 4-nitrobenzyl ketone, (*m*-) $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$  (*p*-), in accordance with the rule of alternate polarities. The general conclusion may be drawn that the alternating polar effect of a nitroxyl group cannot be discerned beyond the limits of the conjugated (crotonoid) system of which it forms a part. We had planned the determination of the directive powers of *m*- and *p*-methoxybenzyloxy-groups, but for reasons explained on p. 391 the latter estimation has not yet been made. The *m*-methoxybenzyloxy-group has the directive power 92 (MeO, 100;  $\text{CH}_2\text{Ph} \cdot \text{O}$ , 113) and it will suffice to note at this stage that the result is in harmony with the effect which a *m*-methoxy-group has in enhancing the ionisation\* constants of some substituted benzoic acids (*e.g.*, anisic acid,  $K = 3.2 \times 10^{-5}$ ; veratric acid,  $K = 3.8 \times 10^{-5}$ ).

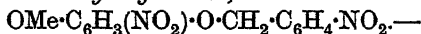
\* The hydrolysis of *p*-iodoxynitrobenzene by alkalis (Vorländer and Büchner, *Ber.*, 1925, 58, 1291) with formation of nitrobenzene and an iodate is a most interesting example of a combined alternating and general effect resulting in the ready production of a complex anion which recovers neutrality by ejecting iodate ion



*p*-Dinitrobenzene does not undergo a similar reaction and this suggests that an important factor in the situation is the heavy iodine atom, which is doubtless capable of adding electrons to its outer shell.

## EXPERIMENTAL.

2-*m*-Nitrobenzyloxyanisole,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ .—*m*-Nitrobenzyl bromide, m. p. 59–60°, was obtained in 96% yield by the action of bromine (32 g.) on a mixture of *m*-nitrobenzyl alcohol (31 g.) and red phosphorus (4 g.). A mixture of guaiacol (10 g.), *m*-nitrobenzyl bromide (17 g.), and alcoholic sodium ethoxide (430 c.c. of 0.5*N*) was refluxed for 1.5 hours, and the solid that was precipitated by addition of water was dried and crystallised from alcohol and then twice from light petroleum; it formed small, pale yellow needles, m. p. 47.5–48° (Found: C, 64.8; H, 5.0; N, 5.7.  $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$  requires C, 64.8; H, 5.1; N, 5.4%).

4-Nitro-2-*m*-nitrobenzyloxyanisole,

The guaiacol carbonate process for the preparation of 5-nitroguaiacol, for some unascertained reason, gave very poor results in this series of experiments and we therefore obtained the substance by the nitration of acetylguaiacol and subsequent hydrolysis (Paul, *Ber.*, 1906, 39, 2779). The ether of the nitroguaiacol was prepared by the method described for the *m*-nitrobenzylation of guaiacol, except that the reaction mixture was boiled for 2 hours. The substance was crystallised from acetic acid and then twice from alcohol, separating in almost colourless, microscopic plates, m. p. 164.5–165° (Found: C, 55.4; H, 4.3.  $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2$  requires C, 55.3; H, 4.0%). All the *m*-nitrobenzyloxy-derivatives were more readily soluble in organic solvents than the corresponding *p*-nitrobenzyloxy-compounds.

5-Nitro-2-*m*-nitrobenzyloxyanisole.—The potassium salt of 4-nitroguaiacol which separates from the product of hydrolysis of 4-nitroveratrole (Pollecioff and Robinson, *J.*, 1918, 113, 645) proved to be homogeneous and was brought into reaction with an equivalent quantity of *m*-nitrobenzyl bromide in boiling alcoholic solution (400 c.c. for 12 g. of the salt) during 1.25 hours. The crude product, m. p. 140°, was twice recrystallised from alcohol, separating in colourless, microscopic plates, m. p. 140.5–141.5° (Found: C, 55.5; H, 4.2%).

*Method of Determination of Freezing Points.*—The material was placed in a thick-walled test-tube (8.5 × 1.5 cm.) provided with a standard Anschütz thermometer (graduated in fifths of a degree, but capable of being read accurately with the aid of a telescope to the nearest 0.05°) and a stirrer of stout silver wire. This vessel was surrounded by an air-jacket and the whole could be heated or cooled in a covered bath of sulphuric acid. The substances to be tested were finely powdered and dried for 10–12 hours at temperatures a few degrees below their m. p. About 1.3 g.

usually sufficed to cover the bulb of the thermometer. The temperature of the outer bath was kept at 20° above the m. p. of the material until this was completely fluid and thereafter at 2° below the f. p., which was ascertained in a rough preliminary experiment or by extrapolation. The liquid in the inner tube was slowly stirred until its temperature was 1.5–2° below the true f. p.; crystallisation was then induced by more vigorous stirring or by scratching; the temperature then rose to a maximum and remained at that temperature, the f. p., for 0.5–3 minutes, slow stirring being continued. In the neighbourhood of the eutectic, the degree of supercooling had a considerable effect on the observed f. p. and, on the other hand, as the mixture approached the eutectic it was less difficult to induce crystallisation. In every case several determinations of each f. p. were made and the mean of the most trustworthy values, the extreme variation not exceeding 0.3°, was calculated. It is not good practice to take the highest value and ignore the remainder, since this high value may have been obtained by some deviation from standard procedure.

*Mixtures of 4-Nitro-2-m-nitrobenzyloxyanisole and  
5-Nitro-2-m-nitrobenzyloxyanisole.*

% 5-nitro-isomeride.	F. p.	% 5-nitro-isomeride.	F. p.
0.0	165.3°	50.2	137.0°
11.47	160.35	55.0	130.9
20.56	156.0	60.1	128.7
29.77	151.4	65.5	129.1 (?)
34.85	148.45	70.3	127.5
39.59	145.1	80.7	133.5
45.47	140.55	92.0	139.1
50.19	136.7	100.0	142.65
54.44	132.2		

Obtained by adding the 5-nitro-isomeride to the 4-nitro-isomeride.

Obtained by adding the 4-nitro-isomeride to the 5-nitro-isomeride.

*Nitration of 2-m-Nitrobenzyloxyanisole.*—The ether (2.170 g.) dissolved in pure acetic acid (25 c.c.) was nitrated by the addition of boiled nitric acid (10 c.c.; *d* 1.42) in one portion, the mixture being mechanically stirred and efficiently cooled by water at 14°. Subsequent operations were exactly the same as those described below in the case of the *p*-nitrobenzyloxy-isomeride. The yield was 98.4% of that theoretically possible and in this case the correction applied to the f. p. was + 0.1°. The corrected f. p. of the nitration product (A) was 145.1° and from the graph this is found to correspond to 39.6% of the 5-nitro-isomeride (Lagrange interpolation formula—39.7%). The corrected f. p. of a mixture (B) of 1.2372 g. of (A) and 0.2520 g. of the 4-nitro-isomeride was 149.65°. From the graph this corresponds to 32.7% of the 5-nitro-isomeride (L.I.F.—32.9%) and hence (A) contained 39.4% (39.6%) of the

5-nitro-isomeride. The best value for the % of 5-nitro-2-*m*-nitrobenzyloxyanisole in the nitration product appears to be 39.6. Hence the directive power of the *m*-nitrobenzyloxy-group is 67. This was confirmed by taking 0.9579 g. of (B) and adding 0.2808 g. of the 5-nitro-isomeride, thus bringing the % of the latter to 48.1. From the graph, the f. p. should be 138.4° (Found: 138.2°).

*Mixtures of 4-Nitro-2-p-nitrobenzyloxyanisole and 5-Nitro-2-p-nitrobenzyloxyanisole.*—The compounds were obtained exactly like the isomerides and in excellent yields. They were crystallised thrice from benzene and obtained in pale yellow, flat needles, sparingly soluble in most organic solvents. The 4-nitro-isomeride has m. p. 167—168° (Found: C, 55.5; H, 4.0.  $C_{14}H_{12}O_6N_2$  requires C, 55.3; H, 4.0%) and the 5-nitro-isomeride has m. p. 163.5—164.5° (Found: C, 55.3; H, 4.1%).

% 5-nitro-isomeride.	F. p.	% 5-nitro-isomeride.	F. p.
0.0	168.3°	49.4	139.3°
6.00	165.6	55.0	138.4
18.76	159.25	58.9	140.8
27.86	154.55	63.2	144.2
40.48	146.9	71.7	150.05
49.60	139.5	76.3	152.8
		83.8	157.0
		89.5	160.0
		100.0	165.0

Obtained by adding the 5-nitro-isomeride to the 4-nitro-isomeride.

Obtained by adding the 4-nitro-isomeride to the 5-nitro-isomeride.

*Nitration of 2-p-Nitrobenzyloxyanisole.*—The *p*-nitrobenzyl ether of guaiacol was obtained like the *m*-nitrobenzyl ether and crystallised from alcohol in pale yellow, glistening leaflets, m. p. 63.5° (Found: C, 64.9; H, 5.0.  $C_{14}H_{13}O_4N$  requires C, 64.8; H, 5.1%). The substance is readily soluble in ether, benzene, chloroform, or acetic acid, sparingly soluble in cold methyl or ethyl alcohol and in hot light petroleum. Lyman and Reid (*J. Amer. Chem. Soc.*, 1920, 42, 615) quote the m. p. (63.6°) of the substance but give no further details. A solution of the ether (3.4 g.) in acetic acid (30 c.c.) was mechanically stirred, cooled in ice, and boiled nitric acid (3 c.c.;  $d$  1.42) mixed with acetic acid (3 c.c.) was gradually introduced. After 2 hours, unchanged substance was recovered, whereas 2-benzyloxyanisole was readily nitrated under similar conditions. Next, the theoretical amount of nitric acid was added to an approximately 10% solution of the ether in acetic acid, and the mixture heated on the steam-bath to 90° without a colour change. One drop of nitric acid was then added and in a minute the liquid suddenly became red and in a short time a considerable amount of a yellow solid crystallised. The addition of a second molecular proportion of nitric acid produced no effect and the temperature



was then raised to 100° for 15 minutes, giving a clear solution. Water was added and the product collected, washed, and dried in the air and at 120° for 2 hours (Found: C, 55.2; H, 4.0. Calc.: C, 55.4; H, 4.0%). On analysis (f. p. 145-95°) this material was found to contain 42% of the 5-nitro-isomeride, and this conclusion was confirmed by addition of the 4-nitro-isomeride and the determination of the f. p. of the mixture.

*Nitration at 14°.* Boiled nitric acid (10 c.c.;  $d$  1.42) was added to a stirred solution of the ether (2.422 g.) in acetic acid (30 c.c.) cooled by water at 14°. In about a minute crystallisation occurred without a change in the colour of the liquid, and after 15 minutes water was added and the product collected, washed, and dried at 80-100° for 10 hours. The yield was 99.1% of that theoretically possible. The f. p. of the crude product was 147.0° and in order to apply a correction for traces of impurities the following procedure was adopted. The finely powdered product (1.5 g.) was heated with pure methyl alcohol (10 c.c.) until the latter boiled; the mixture was then cooled, finally in water at 10°. The solid was collected, 10 c.c. of methyl alcohol being employed for washing the flask and an equal volume for washing on the filter. The material dried at 100° for 1 hour lost very little weight and had f. p. 147.2°. A repetition of the process gave a mixture, f. p. 147.0°. Hence the corrected f. p. of the nitration product is 147.4°. From the graph we find that the corresponding % of the 5-nitro-isomeride is 39.8 (L.I.F.—39.8). The corrected f. p. of a mixture of the nitration product (1.1706 g.) and the 4-nitro-isomeride (0.2419 g.) is 152.0°. Using the interpolation formula, this corresponds to 32.5% of the 5-nitro-isomeride or 39.2% of the 5-nitro-isomeride in the nitration product. The best value for the composition of the mixture obtained by nitration of 2-*p*-nitrobenzyloxyanisole is 4-nitro-2-*p*-nitrobenzyloxyanisole 60.5% and 5-nitro-2-*p*-nitrobenzyloxyanisole 39.5%, whence the directive power of the *p*-nitrobenzyloxy-group is 67. On this assumption, the f. p. of a mixture of the nitration product (0.3842 g.) and the 5-nitro-isomeride (0.7388 g.) should be 154.5° on a branch of the curve not previously employed (Found: 154.25°). An artificial mixture of the two isomerides containing 39.5% of the 5-nitro-isomeride had f. p. 147.25° [Found: Nitration product, f. p. 147.0°; f. p. (corr.) 147.4°].

2-*m*-Methoxybenzyloxyanisole.—Guaiacol (4.9 g.) and *m*-methoxybenzyl bromide (8 g.) (Lapworth and Shoesmith, J., 1922, 121, 1392) were added to a solution of sodium ethoxide (from 0.9 g. of sodium) in 95% alcohol (300 c.c.), and the mixture heated in the steam-bath for 10 minutes. The product was isolated by extraction

with ether after addition of water, and 4.0 g., b. p. 220°/22 mm., m. p. 28—31°, were obtained. By crystallisation from light petroleum the m. p. was raised to 31.5° (Found: C, 74.0; H, 6.5.  $C_{15}H_{16}O_3$  requires C, 73.7; H, 6.6%).

4-Nitro-2-m-methoxybenzyloxyanisole, crystallising from alcohol in short, pale yellow, glistening needles, m. p. 116—117° (Found: C, 62.2; H, 5.4.  $C_{15}H_{15}O_5N$  requires C, 62.3; H, 5.2%), and 5-nitro-2-m-methoxybenzyloxyanisole, crystallising from alcohol in very pale yellow, slender needles, m. p. 98.5—99.5° (Found: C, 61.8; H, 5.5%), were prepared by methods closely resembling those employed for the nitrobenzyl ethers of 5- and 4-nitroguaiacols. The yields were good.

Mixtures of 4-Nitro-2-m-methoxybenzyloxyanisole and 5-Nitro-2-m-methoxybenzyloxyanisole.—The following freezing points were observed, the first number of each pair indicating the percentage of the 5-nitro-isomeride in the mixture: 0.0, 114.85° (1); 11.78, 109.8° (2); 18.57, 106.8° (3); 21.52, 105.3° (4); 31.00, 100.35° (5); 34.20, 98.3° (6); 41.55, 93.1° (7); 50.20, 85.6° (8); 53.91, 82.5° (9); 62.23, 75.2° (10). In applying the Lagrange interpolation formula, the values (1), (2), and (3) were ignored, because in these cases supercooling to the extent of 3° or 4° was necessary. A smooth curve can be drawn through points corresponding to the values (1) to (9) inclusive, and (10) is probably on the other side of the eutectic.

Nitration of 2-m-Methoxybenzyloxyanisole.—The nitration was carried out like that of 2-p-nitrobenzyloxyanisole, except that the temperature was 0° and the flask was kept over-night in melting ice. The yield from 1.9642 g. of the ether was 2.3020 g. (99.0%) and the pale yellow, dry product had m. p. 78—94° (Found: C, 62.4; H, 5.3; N, 5.3. Calc.: C, 62.3; H, 5.2; N, 4.8%). The f. p. of the nitration product was 87.05°, whilst mixtures of the nitration product (1.6128 g.) with 0.2398 g. and 0.3608 g. of the 4-nitro-isomeride froze at 92.85° and 95.4°, respectively. Careful examination of these figures by graphical and algebraic methods, taking into consideration the fact that the f. p. 92.85° is close to a determined point (7) 93.1°, shows that the best value for the composition of the nitration mixture is 48.0% of 5-nitro-2-m-methoxybenzyloxyanisole and 52% of 4-nitro-2-m-methoxybenzyloxyanisole. The directive power of the *m*-methoxybenzyloxy-group is accordingly 92.

2-p-Methoxybenzyloxyanisole.—A solution of anisyl alcohol (5 c.c.) in benzene (30 c.c.) was saturated with hydrogen chloride. The reaction was very rapid. The solution decanted from the aqueous layer was dried by calcium chloride and, the excess of hydrogen

chloride having been removed in a current of dry air, added to a boiling solution of sodium ethoxide (from 1.0 g. of sodium) and guaiacol (6.5 g.) in absolute alcohol (300 c.c.); the mixture was then refluxed for 1.5 hours. The neutral ether, isolated in the usual manner, crystallised from light petroleum in rosettes of white needles, m. p. 94—96° (Found: C, 73.4; H, 6.5.  $C_{15}H_{16}O_3$  requires C, 73.7; H, 6.6%). Despite repeated efforts, satisfactory conditions for the nitration of this compound could not be established. It has not, therefore, been possible to make use of the data recorded below.

*4-Nitro-2-p-methoxybenzyloxyanisole.*—This substance, prepared like the 5-nitro-isomeride described below, was crystallised from alcohol and then repeatedly from light petroleum, separating in very pale yellow, glistening needles, m. p. 129—130° (Found: N, 4.9.  $C_{15}H_{15}O_5N$  requires N, 4.8%).

*5-Nitro-2-p-methoxybenzyloxyanisole.*—The *p*-methoxybenzylation of 4-nitroguaiacol was carried out in the usual manner, with *p*-methoxybenzyl bromide, but the yield was poor. After crystallisation from aqueous alcohol the substance melted at 108° with softening at 100°. Better results were obtained by the following method. Anisyl alcohol (4 c.c.) was converted into chloride in benzene solution as described above, and the liquid decanted from the aqueous layer shaken vigorously for one hour with a solution of the potassium salt (10 g.) of 4-nitroguaiacol in dilute aqueous sodium hydroxide (300 c.c.). The neutral product was extracted with ether, isolated, and crystallised from alcohol and then from light petroleum, separating in pale yellowish-brown, short needles, m. p. 109° with slight softening at 100° (Found: C, 62.2; H, 5.4.  $C_{15}H_{15}O_5N$  requires C, 62.3; H, 5.2%).

Mixtures of the 4- and 5-nitro-2-*p*-methoxybenzyloxyanisoles had the following f. p., the first number of each pair indicating the percentage of the 4-nitro-isomeride: 0.0, 107.8°; 7.01, 103.7°; 19.14, 96.0°; 21.97, 93.4°; 23.20, 91.05°; 29.32, 85.75°; 38.11, 82.2°; 43.64, 91.05°. In this case, it was necessary to resort to seeding, as otherwise the degree of supercooling required was 3° or more.

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LI.—*The Relative Directive Powers of Groups of the Form RO and RR'N in Aromatic Substitution. Part III. The Nitration of some p-Alkyloxy-anisoles.*

By ROBERT ROBINSON and JOHN CHARLES SMITH.

THE nitration of quinol dialkyl ethers in cold acetic acid solution results in an almost theoretical yield of the pure mononitro-derivatives and the composition of the product can therefore be determined with considerable accuracy by the method of thermal analysis. Satisfactory methods for the preparation of 2-nitro-4-methoxyphenol and 3-nitro-4-methoxyphenol and of the ethyl, propyl, and *p*-nitrobenzyl ethers of each of these substances have been devised and the f. p.'s of mixtures of the isomeric pairs of nitroquinol dialkyl ethers have been determined. Examination of the products of nitration of quinol methyl ethyl ether, quinol methyl propyl ether, and quinol methyl *p*-nitrobenzyl ether with the aid of the diagrams so obtained shows that the directive powers of ethoxyl and propoxyl relative to methoxyl are higher than those observed in the catechol series, whilst the *p*-nitrobenzyloxy-group is weaker in the quinol than in the catechol series. Furthermore, whereas propoxyl is weaker than ethoxyl in the catechol series, it is now found to be stronger than ethoxyl in the quinol series. The theoretical implications of these results are discussed in the following communication.

EXPERIMENTAL.

*2-Nitro-4-methoxyphenol.*—The product (90% yield) of the action of nitric acid (1 mol.; *d* 1.42) on quinol dimethyl ether dissolved in acetic acid at 30° had m. p. 71.5° and was homogeneous (Mühlhauser, *Annalen*, 1881, 207, 253, gives 71.5°, and Vermeulen, *Rec. trav. chim.*, 1905, 25, 12, gives 72—73°, as the m. p. of nitroquinol dimethyl ether). After reduction and attempted condensation with phenanthraquinone, no phenazine could be obtained and consequently 2:3-dinitroquinol dimethyl ether, one of the products of the further nitration of nitroquinol dimethyl ether (Nietzki and Pechberg, *Ber.*, 1890, 23, 1211), was not present. The nitrations examined quantitatively in the course of this work were conducted at a lower temperature and it may be safely concluded that no dinitro-derivatives were produced. Under the following conditions, the hydrolysis of nitroquinol dimethyl ether gives a 96% yield of recrystallised 2-nitro-4-methoxyphenol (compare Kauffmann and Fritz, *Ber.*, 1910, 43, 1215; Pollecoff and Robinson, *J.*, 1918, 113,

647). A mixture of nitroquinol dimethyl ether (40 g.), sodium hydroxide (80 g.), and water (700 g.) was refluxed in a copper flask heated in an oil-bath for 54 hours, the liquid being agitated by means of a moderately rapid stream of air. Water (400 c.c.) was then added, the condenser removed, and boiling continued for 30 minutes or until the issuing steam condensed to clear drops on a test-tube filled with cold water. The mixture was cooled to about 60°, acidified with hydrochloric acid, and distilled in a current of steam. The product was collected, dried, and crystallised from light petroleum, separating in red prisms, m. p. 79—80°.

2-Nitro-4-methoxyphenol is also the product of the hydrolysis of nitroquinol dimethyl ether by means of hydrobromic acid. Combined with the fact that nitroveratrole under similar conditions gives 5-nitroguaiacol (Cardwell and Robinson, J., 1915, 107, 255), this indicates the order  $o > m > p$  for the influence of a nitro-group on the ease of hydrolysis of methoxyl by acids. A mixture of nitroquinol dimethyl ether (5 g.) and saturated aqueous hydrobromic acid (15 g.) was heated on the steam-bath for 6 hours. Subsequently 2-nitro-4-methoxyphenol (3.0 g.), m. p. 72—74° (recrystallised, m. p. 79—80°), and nitroquinol (0.5 g.), m. p. 132°, were isolated and identified. The theory of the hydrolysis of methoxyl groups by acids is necessarily complex. In the Friedel-Crafts reaction with phenol ethers the order of influence of the carbonyl group on the ease of hydrolysis of methoxyl is  $o > p > m$ . On the other hand, in euxanthone diethyl ether, we find  $m > o$ , in harmony with the nitroveratrole case. In contrast, the hydrolysis of phenolic ethers by alkaline solutions, as affected by the positions of groups like nitroxyl, gives uniform results— $o, p > m$ .

*Quinol Monomethyl Ether.*—The method of Ullmann (*Annalen*, 1903, 327, 116) for the semi-methylation of quinol was found to give poor yields and the following process was adopted after numerous trials. A solution of quinol (110 g.) in sodium hydroxide (100 g.) and water (700 c.c.), contained in a flask filled with hydrogen, was cooled to 12° and vigorously shaken after the addition of neutral methyl sulphate (120 c.c.) in one portion. After about 5 minutes the mixture was cooled and the dimethyl ether collected (33 g., m. p. 56°). The filtrate and washings were acidified with hydrochloric acid and cooled to about 8° for about 1 hour, thereafter the monomethyl ether was collected, washed with ice water, and dried (45 g., m. p. 52—54°). The aqueous solution was extracted with ether and the residue after evaporation of the solvent yielded to benzene a further 30 g. of less pure quinol monomethyl ether, m. p. 41—46°. For our purposes, it was necessary to ensure the absence of quinol from the product. The material was dissolved

in benzene and any quinol which crystallised was separated; the solution was then distilled and a product, m. p. 53—54°, collected at 243—246°. This was redissolved in benzene, and the solution repeatedly shaken with small quantities of cold water. The ether was then again distilled, b. p. 243—244°, m. p. 56°. No coloration was developed in alkaline solution in contact with air. The substance crystallised from light petroleum has m. p. 56°, but when heated to about 200° and quickly cooled, the m. p. is 53°, changing in a week or two to 55°. Crystals, m. p. 56°, also change on keeping and the m. p. becomes 55°. Although these changes are small, the phenomenon is a real one.

*Ethyl p-Methoxyphenyl Carbonate.*—Ethyl chloroformate (95 c.c.) was added, with shaking and cooling in running water, to a solution of quinol monomethyl ether (124 g.) in water (300 c.c.) and sodium hydroxide (40 g.), and after 30 minutes the product was isolated by means of ether. The yield of a colourless, readily crystallising oil, b. p. 157°/17 mm., was 186 g. (93%). As traces of quinol monomethyl ether might have been produced in the distillation, the substance was washed with 0.05*N*-sodium hydroxide, dilute hydrochloric acid and water, and finally dried in a vacuum. The large, prismatic crystals had m. p. 21° (Found: C, 61.1; H, 6.2.  $C_{10}H_{12}O_4$  requires C, 61.2; H, 6.2%). This ester is rather stable, 5 minutes' treatment with boiling 10% aqueous sodium hydroxide being necessary to effect complete solution.

*Ethyl 3-Nitro-4-methoxyphenyl Carbonate,*  
 $OMe \cdot C_6H_3(NO_2) \cdot O \cdot CO_2Et$ .—

Nitric acid (25 c.c.; *d* 1.52) was added to a solution of ethyl *p*-methoxyphenyl carbonate (25 g.) in acetic acid (25 c.c.), and the mixture heated on the steam-bath until the onset of a vigorous reaction manifested by the copious evolution of red fumes and a rise of temperature to 103°. After being maintained at 100° for 6 minutes, the liquid was cooled, water added, and the solid collected, washed, and dried (27.5 g. or 90%). The m. p. was 66°, and was raised only to 66.5° by crystallisation from light petroleum (Found: C, 49.7; H, 4.9; N, 5.9.  $C_{10}H_{11}O_6N$  requires C, 49.8; H, 4.6; N, 5.8%). Slightly impure specimens are pale yellow and give a violet coloration with cold aqueous sodium hydroxide.

*3-Nitro-4-methoxyphenol.*—This substance, previously prepared by Klemenc (*Monatsh.*, 1914, 35, 91) from its acetyl derivative, is best obtained in the following manner. A mixture of ethyl 3-nitro-4-methoxyphenyl carbonate (10 g.), sodium hydrogen carbonate (4 g.), methyl alcohol (17 c.c.), and water (17 c.c.) was boiled under reflux for 15 minutes, and the methyl alcohol then distilled from

the solution. The cooled, red liquid was acidified with hydrochloric acid; the yellow oil obtained quickly crystallised (6.7 g. or 95%). The m. p. was 97—99°, and 98—100° after crystallisation from benzene. The substance is dimorphous and when melted and suddenly cooled it solidifies to an orange mass which in a few seconds changes with a crackling sound to yellow needles. In one experiment the temperature rose to 99°. The phenomenon is readily observed in a capillary tube and the unstable modification appeared to melt at about 85°. The potassium salt of this nitrophenol immediately after drying is violet and readily soluble in acetone but, when kept for some days or ground in a mortar, it becomes crimson and sparingly soluble, even in boiling acetone. The whole point of the method adopted for the preparation of this substance resides in the avoidance of the use of powerful alkaline reagents in the hydrolysis, since the methoxyl in the *o*-position to the nitro-group is readily attacked, and even by hot sodium carbonate to an extent which would vitiate our results.

*3-Nitro-4-ethoxyanisole*.—2-Nitro-4-methoxyphenol (10 g.) was treated in alcoholic solution with potassium ethoxide (from 2.34 g. of potassium), and after the solvent had been evaporated the red potassium salt was dried at 130° in a vacuum for 2 hours. It was then mixed with absolute alcohol (50 c.c.) and ethyl iodide (9 c.c.) and heated in a pressure bottle at 100° for 3 hours. The alcohol was removed by distillation and the product washed with successive quantities of 1% aqueous sodium hydroxide and with water, collected and dried (10.3 g. or 86%). The crude product had m. p. 38—39° and after crystallisation from methyl alcohol and from light petroleum the substance was obtained in short, yellow prisms, m. p. 39.5° and f. p. 39.0° after drying in a vacuum at 100° for 1 hour (Found: C, 54.6; H, 5.7; N, 7.2.  $C_9H_{11}O_4N$  requires C, 54.8; H, 5.6; N, 7.1%).

*2-Nitro-4-ethoxyanisole*.—A solution of potassium ethoxide (from 1.95 g. of potassium) in alcohol\* (15 c.c.) was added to one of 3-nitro-4-methoxyphenol (8.45 g.) in alcohol (20 c.c.), and after the introduction of ethyl iodide (5 c.c.) the mixture was boiled under reflux for 1 hour; the original deep red colour had then given place to orange. The isolation was like that of the isomeride described above and there resulted 9.5 g. (95%) of yellow needles, m. p. 36—38.5°. The purest specimens had m. p. 37—39°, f. p. 38.4°, and were obtained by crystallisation from methyl alcohol and light petroleum (Found: C, 54.7; H, 5.8; N, 7.1%). When quickly cooled from

\* In this case, the reaction is relatively facile and the use of ethyl alcohol is not disadvantageous. The ether was also prepared with methyl alcohol as the solvent.

100°, the substance melted sharply at 37°, but 1 hour later the m. p. was 37—39°.

*Freezing Points of Mixtures of 3-Nitro-4-ethoxyanisole and 2-Nitro-4-ethoxyanisole.*—Although these substances have a rapid rate of crystallisation, this is not the case with mixtures of them, especially near the eutectic, and the f. p.'s are ascertained only with great difficulty. In some examples the time taken to reach the maximum temperature after crystallisation had begun was no less than 20 minutes. Accurate standardisation of the procedure was therefore an urgent necessity. The external water-bath was contained in a Dewar vessel, and its temperature maintained 0.5° lower than that of the mixture. The mixture was supercooled 1.5°, nucleated from a trace of solid left on the thermometer stem, and stirred at the rate of 1 revolution per second. The temperature could be estimated to the nearest 0.02°. The eutectic could not be accurately located, since in this region a double f. p. was observed. The following mean values were selected, the first number of each pair indicating the percentage of 3-nitro-4-ethoxyanisole in the mixture: 0.0, 38.4°; 7.8, 34.7°; 18.2, 28.0°; 25.4, 24.35°; 31.6, 21.25°; 38.1, 17.5°; 40.75, 15.9°; 41.5, 14.15°; 43.1, 14.5°; 45.9, 12.1° (14.2°); 48.0, 11.8° (14.1°); 50.6, 13.9°; 57.6, 19.1°; 63.3, 22.3°; 67.8, 24.7°; 68.5, 25.2°; 75.7, 28.8°; 81.0, 31.1°; 84.3, 32.3°; 94.1, 36.3°; 100.0, 39.0°.

As a confirmation a mixture was made of 3-nitro-4-ethoxyanisole (1.0643 g.) and 2-nitro-4-ethoxyanisole (0.6413 g.) and found to freeze at 21.9°. From the graph, 21.9° corresponds to 62.4% of the 3-nitro-isomeride (calc., 62.4%).

*Nitration of 4-Ethoxyanisole.*—Fiala (*Monatsh.*, 1884, 5, 233) has prepared 4-ethoxyanisole and states that its m. p. is 39°. Using pure quinol monomethyl ether and ethyl iodide, b. p. 72.4°, we find that the crystallised product has m. p. 36—37°, b. p. 216—217°/754 mm. (Found: C, 70.9; H, 8.0. Calc.: C, 71.0; H, 8.0%). The nitric acid employed in the nitrations described in this communication had  $d$  1.42 and was distilled and freed from oxides of nitrogen by means of a current of air. The acetic acid also was purified and froze at 16°. A mixture of acetic acid (3 c.c.) and nitric acid (1.77 g.; 1 mol.) was gradually introduced by means of a capillary tube below the surface of a stirred solution of 4-ethoxyanisole (2.91 g.; 1 mol.) in acetic acid (6 c.c.) cooled to 4°. As no change of colour occurred, the temperature was allowed to rise to 6° after about 10% of the acid had been added. A yellow colour developed and the mixture was then cooled to 0—1° and the remainder of the nitric acid added during 20 minutes, after which stirring and cooling at 0° were maintained for 20 minutes. The temperature was then allowed



to reach 10° for 5 minutes. A further molecular proportion of nitric acid dissolved in acetic acid (1.5 c.c.) was introduced with similar precautions, and the mixture at 0° was then diluted with water (60 c.c.) at 2°. After being stirred for a few minutes, the mixture was kept for an hour. The oil had solidified and the clear supernatant liquid could be siphoned away without loss of the product. The material was then washed successively with water (20 c.c.) at 30°, twice with very weak aqueous sodium bicarbonate (10 c.c.) at 30°, and finally thrice with water at 30°. In each case stirring was resorted to and the washings were removed after solidification of the oil by cooling to about 5°. After drying to constant weight (3.565 g., 94.6%) in a vacuum, the specimen (a) was prepared for determination of the f. p. by heating in a vacuum at 100° for 30 minutes (Found: N, 7.2. Calc.: N, 7.1%). Further nitrations of 5 g. of 4-ethoxyanisole in an identical fashion gave 6.28 g. (b; 97%) and 6.23 g. (c; 96%) of the mixed isomerides.

The results of analysis are set out in the following table.

Specimen.	Grams of mixture taken.	Weight of 3-nitro-isomeride added.	F. p.	% of 3-nitro-isomeride indicated.	% of 3-nitro-isomeride in the nitration product.
(a) 1	2.6640	0	21.8°	62.2	62.2
2	—	1.4448	28.6	75.5	62.1
(b) 1	3.6087	0	21.95	62.4	62.4
2	—	1.5058	27.7	73.5	62.4
3	2.4048 of last mixture, f. p. 27.7°	2.2597	33.5	86.5	62.9
(c) 1	3.2733	0	21.9	62.4	62.4
2	—	0.9945	26.4	70.9	62.1
3	—	1.6532	28.4	75.0	62.4
					Mean 62.36

In order to ascertain what change of composition, if any, was entailed in the isolation processes, a mixture of the isomerides, f. p. 23.2°, was dissolved in the appropriate quantities of nitric and acetic acids so as to imitate the result of an actual nitration. Isolation and washing were carried out as described above, but before drying the whole series of operations was repeated. The dried material then froze at 23.4°. Two such treatments therefore only change the f. p. by 0.2° and if it is assumed that one isolation process raises the f. p. by 0.1°, the corrected composition of the product of nitration is 62.2% of the 3-nitro-isomeride and 37.8% of the 2-nitro-isomeride. Hence the directive power of ethoxyl relative to methoxyl (100) is 163 in the quinol series.

*3-Nitro-4-propoxyanisole*,  $\text{OMe-C}_6\text{H}_3(\text{NO}_2)\cdot\text{OPr}^a$ .—The propyl iodide employed in the preparation of this substance and of its isomeride had b. p. 101.2—101.7° (Found: I, 74.7, 74.7. Calc.:

I, 74.7%), and the propyl alcohol also was fractionated—b. p. 96.9—97.9°.

A mixture of 2-nitro-4-methoxyphenol (16.9 g.), potassium propoxide (from 3.85 g. of potassium), propyl iodide (20 c.c.), and propyl alcohol (50 c.c.) was boiled under reflux for 11 hours. The solvent was then removed in a vacuum at 100°, and the residue yielded to ether 10 g. (48%) of a dark brown liquid, m. p. 10-22°. This boiled at 127° under less than 1 mm. pressure and the clear yellow distillate had m. p. 10-35°. Repeated crystallisation from methyl alcohol at -15° raised the m. p. to the constant value of 10.7° (Found: C, 56.9; H, 6.4; N, 6.6.  $C_{10}H_{13}O_4N$  requires C, 56.9; H, 6.2; N, 6.6%). In a second experiment, exactly the same results were obtained.

Attempts to improve the above process by employing the silver salt of the nitrophenol in place of the potassium salt were wholly unsuccessful. The silver salt of 2-nitro-4-methoxyphenol was prepared from the sodium salt and silver nitrate in aqueous solution. The material was dried in a vacuum (Found: Ag, 39.4.  $C_7H_8O_4NAg$  requires Ag, 39.1%) and was remarkably stable towards alkyl iodides. Boiling methyl and ethyl iodides produced no effect in 10 minutes, and the action of boiling propyl iodide alone for 12 hours or in solution in ether, benzene, ethyl acetate, methyl, ethyl or propyl alcohol also gave negative results or very poor results.

*2-Nitro-4-propoxyanisole.*—This ether was obtained in 85% yield by the usual method applied to a methyl-alcoholic solution boiling during 12 hours. In all such processes the solvent chosen should be such that alcoholysis of alkyloxy-groups in the *o*- or *p*-positions to nitroxyl cannot introduce impurities. The pure substance, crystallised from methyl alcohol and from light petroleum, has f. p. 32.0° (31.98° in a second preparation) (Found: C, 57.0; H, 6.4; N, 6.7%).

*Mixtures of 3-Nitro-4-propoxyanisole and 2-Nitro-4-propoxyanisole.*

—The following values of the f. p.'s were employed for the construction of a graph, and the first number of each pair indicates the percentage of 2-nitro-4-propoxyanisole in the mixture: 100.0, 32.0°; 95.9, 30.55°; 92.6, 29.5°; 86.5, 27.45°; 80.5, 25.1°; 74.9, 22.9°; 68.6, 20.2°; 63.7, 18.0°; 57.5, 15.0°; 53.1, 12.8°; 48.0, 10.35°. The readings for the mixtures containing less than 48% of the 2-nitro-isomeride were too indefinite to be of practical value.

*Nitration of 4-Propoxyanisole.*—4-Propoxyanisole (Fiala, *Monatsh.*, 1884, 5, 234) was obtained in 85% yield in the usual manner and has b. p. 135°/15 mm. and m. p. 26—27°. The nitration was carried out in precisely the same way as that of 4-ethoxyanisole but, as the product was a liquid at 0°, it was necessary after the washings to allow the complete settling of the droplets before removing the

supernatant fluid. The washed product was siphoned with the aid of methyl alcohol through a Pregl micro-filter into a weighed tube, and the methyl alcohol and water were removed by a current of filtered air at 50° and finally at 110° in a vacuum. In two experiments (a) and (b) the yields were 97% and 98%, respectively [Found in (a): N, 6.7. Calc.: N, 6.6%]. The results of the analysis are tabulated below.

Specimen.	Grams of nitration product.	Weight of 2-nitro-isomeride added.	F. p.	% of 2-nitro-isomeride indicated.	% of 3-nitro-isomeride in the nitration product.
(a) 1	1.1478	0.6043	15.1°	58.0	64.1
2	—	1.0971	19.5	67.1	64.3
3	—	1.6141	22.25	73.2	64.5
(b) 1	1.0771	0.6128	15.6	58.9	64.5
2	—	0.9326	18.85	65.6	64.2
3	—	1.2782	21.05	70.5	64.5
					Mean 64.35

As a check the following experiment was carried out. A mixture of 2-nitro-4-propoxyanisole (1.5173 g.) and 3-nitro-4-propoxyanisole (0.5560 g.) containing 73.2% of the former isomeride was made and this was found to have f.p. 22.25°, agreeing with the value read from the graph. This mixture (0.6 g.) added to that (a 3) of the same f. p. mentioned in the above table (1.0 g.) gave a product, f.p. 22.25°.

Corresponding to the above results, the directive power of the *n*-propoxy-group in the quinol series is 180.

**3-Nitro-4-*p*-nitrobenzyloxyanisole.**—2-Nitro-4-methoxyphenol (1.06 mols.), potassium propoxide (1.04 mols.), and *p*-nitrobenzyl bromide (1 mol.) were employed in the preparation of this substance in boiling propyl-alcoholic solution. The yield was 98% of the theoretical calculated on the *p*-nitrobenzyl bromide employed. The substance crystallises from benzene in yellow needles, m. p. 153°, f. p. 152.8° (Found: C, 55.3; H, 4.0; N, 9.2.  $C_{14}H_{12}O_6N_2$  requires C, 55.2; H, 4.0; N, 9.2%).

**2-Nitro-4-*p*-nitrobenzyloxyanisole** was prepared in the usual manner in methyl-alcoholic solution and the yield was 96%. After recrystallisation from benzene, the substance was heated at 100° for an hour; it then melted at 120–125° with sudden evolution of benzene. After heating in a vacuum at 130–135° for 30 minutes in a slow current of air, the substance melted at 123.5° and froze at 123.0° (Found: C, 55.3; H, 4.3; N, 9.2%). The compound is more sparingly soluble in benzene than its less fusible isomeride.

**Mixtures of 3-Nitro-4-*p*-nitrobenzyloxyanisole and 2-Nitro-4-*p*-nitrobenzyloxyanisole.**—The outer bath of the cryometer was a large beaker of sulphuric acid. The following values of the f. p. were employed in the analysis below and the first number of each

pair represents the percentage of 2-nitro-4-*p*-nitrobenzyloxyanisole in the mixture: 100.0, 123.0°; 93.9, 120.25°; 87.9, 117.5°; 83.65, 115.65°; 78.2, 112.95°. The corresponding curve is almost a straight line. Nearer to the eutectic it was not found possible to obtain concordant readings, but the following mean values indicate the form of the curve: 74.25, 111.5°; 70.2, 109.9°; 67.6, 109.0°; 66.7, 108.4°; 59.8, 111.6°; 55.7, 114.4°; 49.4, 123.0°.

4-*p*-Nitrobenzyloxyanisole.—*p*-Methoxyphenol (1.05 mols.), potassium hydroxide (1.02 mols.), and *p*-nitrobenzyl bromide (1 mol.) in boiling methyl-alcoholic solution gave a 95% yield of the ether. The substance is sparingly soluble in cold methyl or ethyl alcohol, readily soluble in benzene, and crystallises from ethyl alcohol in large, yellow prisms, m. p. 87.5° (Found: C, 64.7; H, 5.1; N, 5.4.  $C_{14}H_{13}O_4N$  requires C, 64.8; H, 5.1; N, 5.4%).

In view of the interest which has been evinced in regard to the bright yellow colour of nitroquinol dimethyl ether, it should be noted that this quinol methyl *p*-nitrobenzyl ether is more intensely coloured than either of the nitroquinol methyl *p*-nitrobenzyl ethers. This clearly indicates that the colour of nitroquinol dimethyl ether is due, not to any quinonoid rearrangement, but to the interaction of the *p*-dialkyloxybenzene nucleus and the nitroxyl functioning independently. The direct attachment of the nitro-group to the quinol nucleus depresses its reactivity and should have a bathochromic effect.

Nitration of 4-*p*-Nitrobenzyloxyanisole.—A mixture of acetic acid (12 c.c.) and nitric acid (12 c.c.; *d* 1.42) was added in one portion to a well-stirred solution of 4-*p*-nitrobenzyloxyanisole (3.0 g.) in acetic acid (30 c.c.). The temperature remained at 22° for 30 seconds, then rose to 25°, and the product began to crystallise. Water (150 c.c.) was added after 15 minutes, and the solid collected after 30 minutes and washed with water. The material (*a*) was dried at 80–90° for 10 hours and then weighed 3.45 g. (98%) (Found: N, 9.3. Calc.: N, 9.2%). A second specimen (*b*) was similarly obtained by nitration at 15–20° in 99% yield, and a third (*c*) by nitration at 16–21° in 99% yield.

Specimen.	Weight of nitration product.	Weight of 2-nitro-isomeride added.	F. p.	% of 2-nitro-isomeride indicated.	% of 2-nitro-isomeride in nitration product.
(a, b, c)	—	—	(109–110.5°)	—	(68–72.5)
(a)	0.7201	0.8143	117.2°	87.1	72.5
	—	1.4556	119.0	91.0	72.8
(b)	1.1561	0.9747	116.25	85.2	72.7
	—	1.7854	118.1	89.2	72.5
(c)	1.0287	0.8636	116.0	84.6	71.7
					Mean 72.4

A mixture of 2-nitro-4-*p*-nitrobenzyloxyanisole (0.9930 g.) and 3-nitro-4-*p*-nitrobenzyloxyanisole (0.1808 g.) contains 84.6% of the 2-nitro-isomeride and has f. p.  $116.0^{\circ}$ , confirming the graph in that region. When 1.17 g. of this mixture was added to 1.4 g. of the mixture (from c) given in the above table as of f. p.  $116.0^{\circ}$ , the f. p. was  $116.0^{\circ}$ . From the above data it appears that the directive power of the *p*-nitrobenzyloxy-group in the quinol series is 38.

An error of  $0.1^{\circ}$  in the f. p. causes an error of 0.2 in the percentage obtained from the graph and one of 0.4 in the calculated percentage composition of the mixture. In the case of ethoxyl an error of  $0.1^{\circ}$  in the f. p. produces an error of 0.27—0.3 in the calculated percentage composition of the nitration product, and in the case of propoxyl an error of  $0.1^{\circ}$  in the f. p. would cause an error of 0.24 in the percentage composition read from the graph and an error of 0.5 in the calculated percentage composition of the nitration product.

The authors wish to express their gratitude to the Royal Commissioners of the Exhibition of 1851 for a scholarship which enabled one of them to take part in the research, and also to the Chemical Society for a grant which has defrayed a part of the cost of the materials employed.

THE UNIVERSITY, MANCHESTER.

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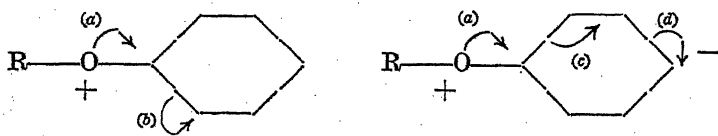
### LII.—*The Relative Directive Powers of Groups of the Forms RO and RR'N in Aromatic Substitution. Part IV. A Discussion of the Observations Recorded in Parts I, II, and III.*

By JAMES ALLAN, ALBERT EDWARD OXFORD, ROBERT ROBINSON, and JOHN CHARLES SMITH.

IN order to avoid misconception as to the point of view adopted as a working hypothesis in this series of memoirs, a brief discussion of the fundamental principles is necessary.

It is recognised that certain ions, for example, those from sodium chloride, exhibit a high affinity for their charge and are relatively inert in the matter of co-valency formation, whereas other ions, for example, those from hydrogen cyanide or benzenediazonium hydroxide, have an intrinsic lower affinity for their charge and are active in the production of new bindings by co-valency. In effect, the former class are chemically inactive, the latter class active and, following Abegg and Bodländer, Kauffmann and Briggs, we can recognise in the two types diffuse and intense valency fields respec-

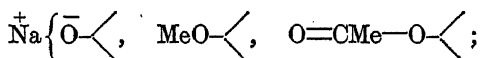
tively. Lapworth has recently contributed a valuable classification of reagents as *anionoid* or *kationoid* according as they behave in the same way as active negative or positive ions (Paper read at the Manchester Literary and Philosophical Society on March 3, 1925; see abstract, *Nature*, **115**, 625). Ethylene, butadiene and benzene are anionoid, their *active* free valency has a negative polar character, and it is obvious that the ethers and amines are even more definitely anionoid. The systems which one of us has called *crotenoid* (Robinson, *J. Soc. Chem. Ind.*, 1925, **44**, 456) are strongly anionoid, the natural character of the unsaturated carbon being reinforced by direct union with an *onium* element. Lapworth points out that, when ethylene polarises, the implication is that the unsaturated carbon with a positive charge is in the more natural or stable condition and is surrounded by a diffuse field. The active unsaturated carbon with a negative charge is in a less natural condition, and this is justly held to be related to the observation that, except  $C_2H^*$ , no hydrocarbon radicals have been observed to occur with a negative charge in Thomson's vacuum tube experiments. Independent of these acute comparisons, the development of the theory of crotenoid systems (Decker, *Ber.*, 1905, **38**, 2893; Hamilton and Robinson, *J.*, 1916, **109**, 1029; Robinson, *ibid.*, p. 1038; *Mem. Manchester Phil. Soc.*, 1920, **64**, 4; Robinson and Robinson, *J.*, 1917, **111**, 958; 1918, **113**, 640; Kermack and Robinson, *J.*, 1922, **121**, 427) required the assumption that the reactive carbon atoms in phenols and amines and their derivatives acquire a negative charge in the course of polarisation, the postulated precedent of all reactions. In the case of a phenol ether the mechanism of activation is represented by the annexed expressions.



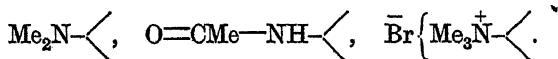
The oxygen, by means of its free electrons, increases its co-valency with the ring  $C_a$  (process *a*).  $C_a$  recovers its normal co-valency by giving up correspondingly electrons to  $C_b$  (process *b*) (*o*-substitution) or by relinquishing  $C_aC_b$  co-valency electrons to  $C_bC_c$  (process *c*).  $C_c$  must then relinquish  $C_bC_c$  co-valency electrons to the sole use of  $C_d$  (process *d*) (*p*-substitution). In the activated form the oxygen is positively charged and is exhibiting oxonium character, a rôle in which it far more closely resembles, in its general stability, the satisfied ions ( $Cl^+$ ,  $Na^+$ ) than does the negatively charged

\* As usual, a group derived from acetylene is exceptional.

carbon atom. The latter is intensely reactive and easily forms new co-valencies (compare *J. Soc. Chem. Ind.*, *loc. cit.*, for the details of the mechanism of diazo-coupling on this hypothesis). This type of activation involves the displacement of electrons in a particular direction, *e.g.*, from left to right in the figures. Furthermore, since the oxygen acquires a smaller negative charge or an actual positive charge, the process must be the more facile the more highly negatively charged is the oxygen atom before the activation. This explains the descending order of reactivity in the series :



and in the series :



In the acetoxy- and acetylamino-groups, conjugation gives the atom attached to the nucleus a positive charge (compare Rây and Robinson, *J.*, 1925, 127, 1618). It remains to add that the aromatic nucleus has a special stability of its own which Armit and Robinson (*J.*, 1925, 127, 1604) consider to be due to the possession of a stable electronic structure, the aromatic sextet. Electronic displacements are resisted by the sextet and it is a fact that the activation of a benzenoid centre in conjunction with any external group is feeble compared with that of an ethenoid complex in similar circumstances. Thus nuclear alkylation by the action of an alkyl halide on a crotenoid base occurs only with the more active aromatic systems. In the course of this investigation our views on the part played by the phenomenon of conjugation in organic chemistry have been more clearly focussed and it now appears possible to classify conjugated systems without arbitrary assumptions. Among the unit reactive groupings from which more complex structures may be derived, especial interest attaches to the highly unsaturated centres \* typified by  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$  ( $\text{C}\equiv\text{N}$ ,  $\text{N}=\text{O}$ , etc.), and  $-\text{O}-$  ( $-\text{NR}-$ ). Of these,  $\text{C}=\text{O}$  alone is kationoid. Certain groupings,  $\text{C}-\text{R}$ , to which definite conditions are attached, must be included. Combining the unsaturated groups two at a time in every possible way, we get :

(1)  $\text{C}=\text{C}-\text{C}=\text{C}$ ; *butadienoid*; polarisation—  $+|\text{C}=\text{C}-\text{C}=\text{C}|^-$ ; reactivity—*anionoid*.

Examples are isoprene, aromatic hydrocarbons.

\* Certain special structures (ketens, acetylenes) are not considered and it is not suggested that the classification is a complete one.

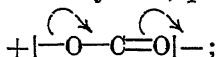
(2)  $\text{C}=\text{C}-\text{C}=\text{O}$ ; *crotonoid*; polarisation—  $+\left|\text{C}=\text{C}-\text{C}=\text{O}\right|^-$ ; reactivity—kationoid.

Examples are methylenemalononic ester, mesityl oxide.

(3)  $\text{C}=\text{C}-\text{O}-$ ; *crotenoid*; polarisation—  $-\left|\text{C}=\text{C}-\text{O}-\right|+$ ; reactivity—anionoid.

Examples are ethyl  $\beta$ -aminocrotonate, dimethylaniline, resorcinol.

(4)  $-\text{O}-\text{C}=\text{O}$ ; neutralised system; polarisation—



reactivity—feebly kationoid at C and special characters (see below).

Examples are esters, amides, dianisylideneacetone.

(5)  $\text{O}=\text{C}-\text{C}=\text{O}$ , *quinonoid*, and (6)  $-\text{O}-\text{O}-$ , *peroxidic*, are heterogeneous systems which we do not propose to discuss.

Many more complex combinations of the unsaturated units are possible and especially it will be recognised that all the systems may be expanded by the inclusion of further  $\text{C}=\text{C}$  groups. In addition there are derived forms of which the following are the most important.

(7)  $\text{O}=\text{C}-\text{C}-\text{X}$ , where X is an atom or group independently capable of separating with a positive charge; *semi-crotonoid*;

polarisation—  $-\left|\text{O}=\text{C}-\text{C}-\text{X}\right|+$ ; reactivity—dissociation; often followed by rearrangement of the negative ion and anionoid character exhibited by the carbon atom previously joined to X. The process is analogous to the dissociation of a carboxylic acid.

Examples are acetone, 2 : 4-dinitrotoluene, ethyl  $\alpha$ -bromoacetate.

(8)  $\text{C}=\text{C}-\text{C}-\text{Y}$ , where Y is an atom or group independently capable of separating with a negative charge; *allyloid*; polarisation—

$+\left|\text{C}=\text{C}-\text{C}-\text{Y}\right|^-$ ; reactivity—kationoid.

Examples are phenyl allyl ether (Claisen and Tietze, *Ber.*, 1925, 58, 275), geraniol.

(9)  $\text{O}-\text{C}-\text{Y}$  occurs in  $\text{MeO}\cdot\text{CH}_2\text{Cl}$ , etc.

*The General Polar Effect.*—Conjugation occurs by virtue of electronic displacements which produce an alternating polar effect\* as

\* An alternating polar effect in a chain  $\text{A}^-\text{B}^+\text{C}^-\text{D}^+\text{E}^-$  does not mean and never has meant either to Lapworth or to Robinson that the atoms are alternately positively and negatively charged. The phrase is taken to imply that evidence exists that in certain reactions, due to separate polarisations, A, C, or E may exhibit anionoid character and, on the other hand, one of the centres B or D may exhibit kationoid character. The alternation of



an inevitable consequence of the laws of valency operating in relation to changes in co-valency. Electronic displacements which do not involve co-valency changes require no alternation and may be continuous but diminishing in degree along a chain (compare Lapworth and Robinson, *Nature*, 1923, 112, 722). Such displacements should occur in almost all types of molecules and will be propagated by electrostatic induction (Lewis, *J. Amer. Chem. Soc.*, 1916, 38, 762; "Valence and Structure of Atoms and Molecules," pp. 84, 143; Thomson, *Phil. Mag.*, 1923, 46, 497; Lowry, *Trans. Faraday Soc.*, 1923, 18, 293; Lucas and Jameson, *J. Amer. Chem. Soc.*, 1924, 46, 2475). We concur \* with Lucas and Moyse (*ibid.*, 1925, 47, 1459), for instance, in their application of the theory to the case of the addition of hydrogen bromide to  $\Delta^2$ -pentene. The general effect of charged centres is obvious and Thomson (*loc. cit.*) has suggested both practical and theoretical methods of estimating the disposition of electrostatic doublets in various types of atomic combinations. In addition, the general effect of a group R can often be estimated by a consideration of the strength of the acid  $R \cdot CO_2H$ . All the evidence goes to show that hydrogen has a greater attraction for electrons than has the methyl group; we shall find it more convenient to express this statement in the converse form. This effect is represented, as in former cases (Malkin and Robinson, *J.*, 1925, 127, 370), by a straight arrow showing the direction in which the electrons are displaced. As an example of the interaction of the two types of electron displacement, we consider the carboxylic

acids  $R \cdot CO_2H$ . The polarisation  $\overset{\text{O}}{\underset{(b)}{\parallel}}\text{C} \overset{\text{O}}{\underset{(a)}{\leftarrow}}\text{H}$  proceeds until the positive charge† on the hydroxyl oxygen increases to such an extent that the proton is weakly held and can be removed by solvent molecules. The two oxygen atoms then divide the negative charge and assume identical functions. The displacement (a) is clearly the more fundamental process, but (b) is, however, a necessary

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stable and less stable octets was suggested by Kermack and Robinson (*loc. cit.*) as a possible, admittedly speculative, explanation of the tendency underlying the exhibition of this property. This suggestion was never intended to be regarded as a *mechanism* of activation, for which Kermack and Robinson retained an electronic translation of the theory of partial dissociation of conjugated complexes as developed by Robinson and Robinson (*loc. cit.*).

\* Except, naturally, in considering that clear cases of the operation of continuous electron displacement dispose of the necessity for recognising the other type of displacement which occurs in conjugated systems.

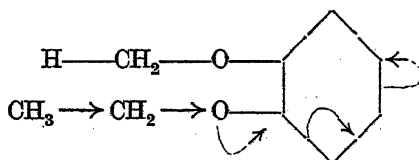
† Positive and negative are taken to mean also less negative and less positive respectively. Similarly, a smaller attraction is relatively a repulsion, and *vice versa*.

accessory in providing a means of adjustment of the disturbed co-valency of the carbon atom.

Contrasting  $R \rightarrow C \begin{smallmatrix} O \\ \parallel \\ OH \end{smallmatrix}$  and  $R' \leftarrow C \begin{smallmatrix} O \\ \parallel \\ OH \end{smallmatrix}$  it is apparent that the group  $R$  in repelling electrons *competes* with  $OH$  and to some extent inhibits the process (a), whilst the opposite is true of a group  $R'$  which attracts electrons. Thus  $R' \cdot CO_2H$  is a stronger acid than  $R \cdot CO_2H$ . The case of the phenols is simpler and again  $R' \cdot OH$  should be a stronger acid than  $R \cdot OH$ . Conjugation  $R \begin{smallmatrix} \curvearrowright \\ \parallel \\ OH \end{smallmatrix} C=O$  is also a factor, weakening an acid. This system does not exclude the consideration of the effect of a steric factor\* (Flürsheim, J., 1909, 95, 718) and is in excellent agreement with the available data.

The whole of the foregoing can be independently justified and we proceed to consider how these principles apply to the results recorded in the preceding communications.

In the ethyl ether of guaiacol we have the condition

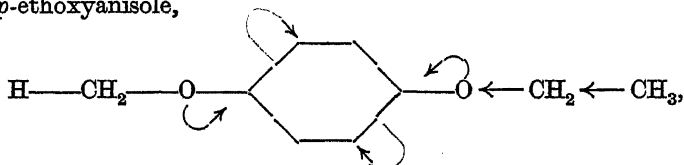


because the methyl group exercises a greater repulsion on electrons than hydrogen does. Therefore the polarisation of the crotenoid system, including the oxygen of the ethoxyl group, is facilitated as compared with the other system, not represented, which includes the oxygen of the methoxyl group. It follows that ethoxyl should have a higher directive power than methoxyl † (Found :  $EtO$ , 135;  $MeO$ , 100). The substitution of methyl for a second hydrogen atom should still further increase the directive power (Found :  $Pr^oO$ , 150). It is very interesting, however, that in the catechol series  $EtO$ , among  $n$ -alkyloxy-groups, appears to reach a maximum directive power (Found :  $EtO$ , 135;  $Pr^oO$ , 128;  $n-C_4H_9O$ , 123). This phenomenon we regard as due to the fact that as the chain lengthens a greater proportion of the general effect is distributed over the molecule and a smaller proportion, therefore, is effective through the attached atoms of the chain. Thus the ratio Directive

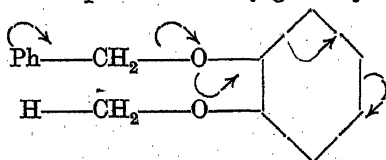
\* Possibly also an electrical effect exercised across the intervening space rather than through the chain.

† The case of  $OH$  itself as against  $OMe$  cannot be considered on similar lines on account of the possibility of ionisation or removal of the proton from  $OH$  by the reagent.

power  $RO/\text{Directive power } MeO$  can be expressed as  $y + a/x + a$ ,\* where  $R$  is a higher alkyl group,  $y$  is its directive power apart from  $a$ ;  $x$  is the directive power of methoxyl apart from  $a$ ,  $a$  is a quantity depending on the general polar effect of the excess methylene groups in  $R - Me$  and is that portion of the effect which, owing to its distribution over the molecule, goes to assist the polarisation of the crotonoid system, including the oxygen of the methoxyl groups. As  $a$  increases, the ratio will approach some minimum value greater than 1. Our results can be interpreted on the assumption that the terminal methyl group of a  $n$ -propyl group exercises a general effect which is largely distributed over the molecule and only to a small extent transmitted through the attached chain. In the series of catechol experiments it is important to observe that the general effect must assist both conjugations, and the interest of parallel experiments in the quinol series is that this is no longer true. Thus in  $p$ -ethoxyanisole,



it is clear that the conjugations of the crotonoid systems themselves involve electronic displacements in opposing directions. The argument used in the catechol series still holds; ethoxyl should have a greater directive power than methoxyl, but if a portion of the general effect of the additional  $CH_2$  of the ethoxyl is distributed, we can write: Directive power of  $EtO/\text{Directive power of } MeO = y' + a'/x' - a'$ . It might accordingly be anticipated that ethoxyl would have a higher relative directive power in the quinol than in the catechol series (Found:  $EtO$  in catechol series, 135;  $EtO$  in quinol series, 163). Furthermore, as  $a'$  increases, the value of the ratio  $(y' + a')/(x' - a')$  must also increase, and the theory, which predicts a lower value for  $Pr^oO$  as compared with  $EtO$  in the catechol series, also requires in the quinol series that  $Pr^oO$  should be greater than  $EtO$  (Found:  $Pr^oO$  in quinol series, 180). In the benzyl ether of guaiacol we encounter one of the postulated conjugated systems (allyloid):



\* The form of this expression is justified if  $x$ ,  $y$ ,  $a$  are taken as representing the number of occasions in unit time on which the different factors concerned lead to effectual polarisations.

In such a case the whole chain is not to be regarded as *one* conjugated system. The allyloid system \* tends to assist the oxygen atom to acquire a negative charge, and this assists the related crotonoid system to function † (Found :  $\text{CH}_2\text{Ph}\cdot\text{O}$ , 113;  $\text{MeO}$ , 100).

In the *m*-methoxybenzyl group (directive power, 92), the methoxyl group has the general effect anticipated on the basis of Thomson's deductions concerning the situation of electrostatic doublets, and the whole group exercises less repulsion on electrons than the methyl group does. This is far more pronounced with *m*- and *p*-nitrobenzyloxy-groups (directive powers, 67). The identity of the directive powers of these two groups was unexpected and led us to adjust our views on conjugation in the direction now indicated. It must not, however, be hastily concluded that the nitro-group produces no alternating effect, even in these experiments, since the fact that *p*-nitrobenzoic acid is slightly stronger than the *m*-isomeride indicates a weak alternate effect. In the *m*-nitrobenzyloxy-group, we might have a slightly stronger general effect and a weaker alternating effect (crotonoid-type) than in the *p*-nitrobenzyloxy-group, and these small variations may balance. However this may be, the results show that if the nitro-group does produce an alternating effect it must be a very small one and this is normal because the reaction examined is one in which the substance exhibits anionoid character and conjugation of nitroxyl with the aromatic nucleus leads to the exhibition of kationoid properties. In the catechol series, for a group like the *p*-nitrobenzyloxy-group we have : Directive power of group/Directive power of  $\text{MeO} = (z - b)/(x - b)$  and in the quinol series the ratio becomes  $(z' - b')/(x' + b')$ . Thus in the quinol series such a group should have a smaller relative directive power than in the catechol series (Found for the *p*-nitrobenzyloxy-group : in the catechol series, 67; in the quinol series, 38). In connexion with these deductions, it is important to notice that there

\* It should be noted that the distribution of affinity in the butadienoid, crotonoid and allyloid systems on our electronic basis coincides with the requirements of Flürscheim's theory, but this is not the case in the crotonoid and semi-crotonoid types.

† The occurrence in some substances of quite complex combinations of general and alternate effects can be foreseen. Thus *p*-isopropoxybenzoic acid should be weaker than anisic acid or even than *p*-*n*-propoxybenzoic acid :



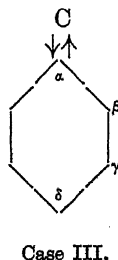
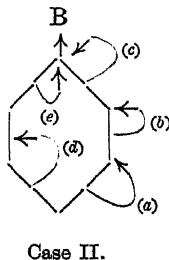
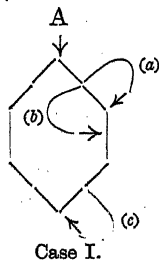
Here we have a general effect reinforcing a crotonoid system the polarisation of which produces a general effect (a), or a conjugation effect (b), or both; these upon influencing the carboxyl as explained above.

are no side reactions to complicate the issue and that in all cases we have measured the whole effective directive power of the groups concerned. Consequently the small differences between  $x$  and  $x'$ ,  $y$  and  $y'$ , and  $z$  and  $z'$  are not likely to affect the validity of our conclusions. We do not claim that the interpretation is more than an approximation to the truth.

The point of view now adopted is one from which the general problem of orientation in aromatic substitution can be surveyed and we regard it as necessary to approach the subject in the following stages, which are of diminishing importance.

- (1) Consideration of the circumstances of the reaction and especially whether the reagent is anionoid or kationoid.
- (2) Consideration of the conjugated systems.
- (3) Consideration of the general effect of attached groups on the conjugated systems.

We will confine ourselves to the cases such that there is no attached group conjugated with the nucleus and the reagent is kationoid ( $\text{Br}_2$ ,  $\text{HNO}_3$ , etc.). In other words, we contemplate a normal benzenoid (butadienoid) system exhibiting anionoid character and wish to deduce from fundamental principles the nature of the effect of attached groups. In the case of a group, A, which repels electrons more than hydrogen does we have the arrangement (I). Here the crowding of electrons



round  $C_a$  will facilitate, by repelling  $C_aC_\beta$  co-valency electrons, the polarisation of that particular butadienoid system which starts with  $C_a$ . The electron will be captured by  $C_\beta$  (process  $a$ ;  $o$ -substitution) or, if not, a  $C_aC_\beta$  co-valency electron will become a  $C_\betaC_\gamma$  co-valency electron (process  $b$ ).  $C_\gamma$ , to recover its normal co-valency, must then correspondingly relinquish an electron to  $C_\delta$  (process  $c$ ;  $p$ -substitution). An alternative statement is that the ring carbon atom around which the density of electrons is greatest most easily becomes the positive end of a conjugated polarised complex. The applications will be obvious—toluene and *tert*-butylbenzene are in the same category. In the case of a group B, which has a *strong*

attraction for electrons (II), it is easy to see in a general way that the circumstances are reversed, but in order to make the argument clear we take an extreme instance such that B has a definite positive charge. The electrical field emanating from B then produces positive electrification in diminishing degree over the portion of the molecule represented. One consequence is that all displacements of electrons in activation will tend to be towards B, and this inhibits para-substitution. Of all the remaining possible displacements (*a*, *b*, *c*, *d*, *e*), that indicated by (*a*) is the most likely to lead to reaction, because reaction depends on the acquirement of a negative charge and of all the carbon atoms which can be activated C<sub>1</sub> has the smallest positive charge. A less degree of electron displacement, therefore, will activate C<sub>1</sub> than will suffice for C<sub>6</sub>. In order of preference we find in this case *m*-substitution, *o*-substitution, *p*-substitution, whilst displacement of the group B is also possible. An alternative statement is that the carbon atom (C<sub>6</sub>) furthest removed from the positive charge is least positive or most negative and most easily acquires a more positive charge and therefore most readily functions as the positively charged end of a polarised ethenoid or butadienoid complex. We cannot lay down any rules in regard to the required strength of the positive charge on B. The nitrogen of the nitro-group is positively charged if we accept the formulation  $\text{=}\overset{\text{I}}{\underset{\text{I}}{\text{O}}}\text{--N=}\overset{\text{I}}{\underset{\text{I}}{\text{O}}}\text{--}$  in which each line represents an electron pair and it would appear that this group is effective even when separated from the nucleus by one carbon atom (Holleman, *Rec. trav. chim.*, 1895, **14**, 121).

Substitution in the *m*-position might also occur in a benzyl-ammonium ion.

The carbon atoms of the carboxyl, carbonyl and trichloromethyl groups can also be regarded as positively charged on the basis of independent evidence. This theory seems to harmonise better than any other which has been advanced with the facts of substitution in polycyclic aromatic groups, but a separate discussion of this subject is necessary. In the case of a group C (III) which in some phases attracts and in others repels electrons we anticipate predominating *o-p*-substitution because the phase in which electrons are repelled provides a favourable opportunity for activation leading to anionoid character, whereas the other phase in no way contributes to activation and in fact inhibits it.

In the case (I) a negative charge is distributed over the nucleus and anionoid character is intensified, leading to ready reaction, whilst in case (II) the distributed positive charge inhibits the substitution of anionoid character. We can in fact estimate the

approximation of a group X to the types A or B by observing the ease of substitution of X-Ph as compared with that of benzene.

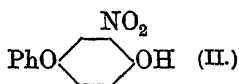
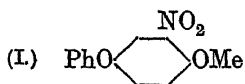
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LIII.—*The Relative Directive Powers of Groups of the Form RO and RR'N in Aromatic Substitution. Part V. The Nitration of p-Methoxydiphenyl Ether.*

By THOMAS RUSSELL LEA and ROBERT ROBINSON.

THE three methoxydiphenyl ethers were prepared with the object of examining quantitatively the products of their fission by potassium, but the reaction proved to be a complex one and its study was deemed unlikely to furnish the desired information. In the course of our experiments, however, an observation was made which has a direct bearing on the subject of the present series. *p*-Methoxydiphenyl ether yields a single nitro-derivative (I) the constitution of which follows from its hydrolysis to *o*-nitro-*p*-phenoxyphenol (II).

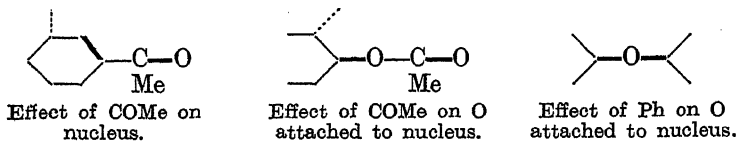


This proves that the directive powers of phenoxy and *p*-methoxyphenoxy are small compared with that of the methoxy group and the result is in harmony with the theoretical conceptions outlined in the preceding memoir. The weak directive powers of the acyloxy and phenoxy groups are undoubtedly due to the same cause, namely, that the oxygen atom is conjugated on both sides.



Using the electrical conductivity analogy, the effect has been described as a "side tracking by a neighbouring system of high capacity" (*Chemistry and Industry*, 1925, 44, 118). On Flürscheim's theory of alternating affinity demand, a similar explanation of the weakness of the phenoxy group could be elaborated, but a consistent application of this hypothesis would appear to suggest that the acetoxy group should have a strong directing influence. Yet *o*-methoxyphenyl acetate is nitrated exclusively in the para-position

with respect to the methoxyl group. The following scheme illustrates this contrast :



### EXPERIMENTAL.

*m*-Methoxydiphenyl Ether.—A mixture of *m*-methoxyphenol (15.5 g.), bromobenzene (15.5 g.), potassium hydroxide (6.2 g.), and copper bronze (0.1 g.) was heated under reflux (oil-bath at 240°) for 2.5 hours. The product was isolated by steam distillation, the excess of bromobenzene being first collected. The benzene extract of the distillate was washed with aqueous sodium hydroxide and water, dried, and distilled finally in a vacuum. The substance, b. p. 175°/20 mm., could not be crystallised (Found: C, 77.9; H, 6.2.  $C_{13}H_{12}O_2$  requires C, 78.0; H, 6.0%). The yield was 19.0 g.

*p*-Methoxydiphenyl Ether.—This compound was prepared by the method described above for the resorcinol derivative and the yield was the same. The substance, b. p. 186°/32 mm., crystallised at -10°, but melted again at room temperature (Found: C, 77.8; H, 6.1%).

3-Nitro-4-methoxydiphenyl Ether (I).—A mixture of nitric acid (15 c.c.; *d* 1.42) and acetic acid (15 c.c.) was gradually added to a solution of *p*-methoxydiphenyl ether (5 g.) in acetic acid (20 c.c.) maintained at about 15° by cooling. Fifteen minutes after the addition of the nitric acid, water was added and the solid collected, washed, and dried (5.8 g.). The substance crystallised from alcohol in pale yellow prisms, m. p. 73—74° (Found: C, 63.7; H, 5.2.  $C_{13}H_{11}O_4N$  requires C, 63.7; H, 4.9%). No other product of the reaction could be isolated. In a similar manner, *o*-methoxydiphenyl ether (Ullmann and Sponagel, *Ber.*, 1905, **38**, 2211) (5 g.) gave 4.9 g. of a solid product which crystallised from alcohol in long, colourless needles, m. p. 70—71° (Found: C, 63.5; H, 4.7%). In this case, however, only 2.8 g. crystallised from alcohol and an oil was precipitated by the addition of water to the alcoholic mother-liquor. It is probable that the product analysed is 3-nitro-6-methoxydiphenyl ether.

2-Nitro-4-phenoxyphenol (II).—3-Nitro-4-methoxydiphenyl ether (4 g.) was hydrolysed by a boiling solution of potassium hydroxide (30 g.) in water (200 c.c.) in a copper flask for 60 hours. The red solution with some red needles in suspension was acidified with hydrochloric acid and the yellow solid, which separated from an



emulsion, was collected, washed, and dried (1.0 g.). The substance crystallises from light petroleum in long, yellow needles, m. p. 51—52° (Found: C, 62.3; H, 4.0.  $C_{12}H_{10}O_4N$  requires C, 62.4; H, 3.9%). The substance gives a bright red potassium salt and when boiled in xylene with potassium carbonate and methyl sulphate yields 3-nitro-4-methoxydiphenyl ether, m. p. 73—74°. Since Borsche (*Ber.*, 1923, 56, [B], 1488) has shown that phenoxy groups in the *o*- or *p*-positions to nitro-groups are more reactive than similarly situated alkyloxy-groups, there can be no doubt in regard to the constitution of the product of nitration of *p*-methoxydiphenyl ether.

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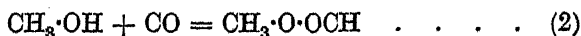
#### LIV.—*The Equilibrium between Methyl Formate and Methyl Alcohol, and Some Related Equilibria.*

By JENS ANTON CHRISTIANSEN.

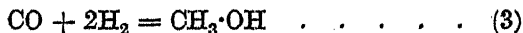
THE announcement that the Badische Anilin- und Soda-Fabrik had succeeded in synthesising methyl alcohol from carbon monoxide and hydrogen attracted great interest. Patart (*J. Ind. Eng. Chem.*, 1925, 17, 430, 859) claimed priority in this invention; but without entering into this discussion it may be mentioned that the process



patented by the author in 1918, combined with the reaction



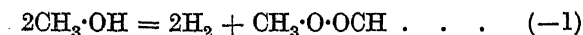
investigated by Stähler (*Ber.*, 1914, 47, 580), was the first which made it possible to prepare methyl alcohol from water gas, although any process by which the reaction



can be carried out without methyl formate as an intermediate product must be of the greatest value.

The author was able to measure the equilibrium constant of reaction (1) by the kind permission of Prof. E. Büllmann, Director of this Laboratory, to whom he wishes to express his thanks. Later, in connexion with a firm in Copenhagen, Mr. Arne Olsen and the author made some measurements of the equilibrium constant of reaction (2). The results of these researches are in this paper: the substance of them was described, with the permission of the firm, in a lecture to the Chemical Society of Copenhagen on October 14, 1924.

Earlier work had shown that when methyl alcohol vapour is passed over reduced copper at 200° it splits up according to the equation



and not, as stated by Sabatier, according to



Before this result was published, Mannich and Geillmann (*Ber.*, 1916, 49, 585) had drawn the same conclusion. As this reaction (—1) did not appear to be complete, a mixture of measured quantities of hydrogen and methyl formate was passed over reduced copper at about 180°, and a considerable decrease in volume observed, showing the occurrence of reaction (1).

To determine the equilibrium, a stream of electrolytic hydrogen, freed from oxygen by means of palladinised asbestos, and dried, was passed at a constant rate (by the use of a pressure regulator and capillary) through a saturator, containing methyl formate, in a thermostat. It then passed through a pipette containing reduced cuprous oxide on asbestos, which was heated in an electric oven, through two absorption tubes, and into a gas burette. The catalyst was reduced with hydrogen *in situ* before the experiment. The absorption tubes were filled with *N*/10-sodium hydroxide. In each experiment, the gas was allowed to escape before reaching the absorption tubes until the rate of flow and the temperatures of the saturator and the oven had been constant for some time. The escape was then stopped and the reaction products were collected. After a suitable time, the absorption tubes were removed and weighed (the hydrogen in them having been replaced by air free from carbon dioxide), and their contents titrated after addition of barium chloride (Winckler's method), so that both methyl alcohol and carbonic and formic acids were determined. The gas was analysed in an Orsat apparatus with platinum capillary. In this way, the amounts of methyl alcohol, methyl formate, hydrogen, carbon monoxide, and dioxide could be estimated. Allowance was made for water lost by evaporation from the absorption tubes, etc.

The equilibrium was also determined by starting with methyl alcohol. This was admitted directly to the catalyst in the oven from a burette through a capillary which was warmed above the b. p. of the alcohol. The results are in Table I, Nos. 1—10 being experiments on reaction (1), Nos. 11—17 on reaction (—1). The temperature of the oven was measured by a standardised thermometer placed outside the catalyst pipette; the error so produced was small, since the rate of flow was slow. The velocities in column 5 are in millimols. of methyl formate or pairs of millimols. of methyl

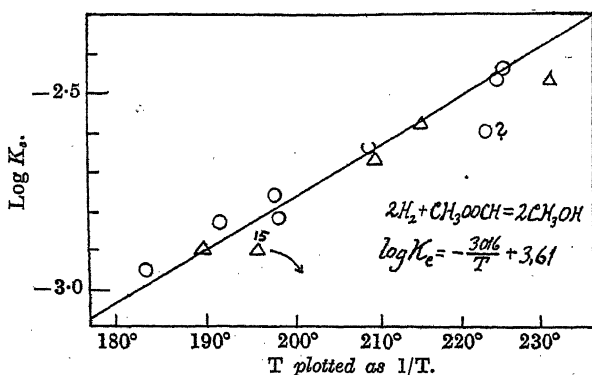
TABLE I.

No.	Temp. of oven.	Pressure of in mm. Hg.	Temp. of water- bath.	Velocity. $\text{CH}_3\text{OH} \cdot \text{CH}_3\text{O} \cdot \text{OCH}_3$ . mmol./hr.	$\text{CH}_3\text{O} \cdot \text{OCH}_3$ . mmol.	$\text{CO}_2$ . mmol.	$\text{CH}_4$ . mmol.	$\text{H}_2$ . mmol.	$\text{CH}_3\text{O} \cdot \text{OCH}_3$ . $\left\{ \begin{array}{l} \text{v. p.} \\ \text{anal.} \end{array} \right.$	$K_1 \times 10^3$ .
1	198.9°	758	13.56°	6.91	8.29	4.38	0.29	5.96	0.912	1.51
2	199.6	773	13.60	8.80	11.59	6.32	0.15	8.60	0.880	1.55
3	198.7	773	13.64	2.79	7.51	5.08	0.22	6.64	0.882	1.50
4	224.8	779	10.60	6.86	5.03	5.04	0.19	8.44	0.876	2.5
5	227.0	779	10.60	1.40	2.53	3.34	0.16	5.65	0.676	3.4
6	197.6	765	10.60	4.16	5.53	3.16	0.13	5.25	0.697	1.75
7	225.5	772	10.60	1.85	2.86	4.68	0.18	7.80	0.687	3.62
8	183.4	776	10.67	5.67	12.00	3.35	0.12	6.98	0.683	1.11
9	192.2	785	10.71	4.29	6.93	2.96	0.11	5.49	0.672	1.47
10	208.3	771	10.70	3.63	4.85	4.09	0.15	6.66	0.693	2.28
11	209.0	785		2.07	5.46	2.64	0.16	7.12	0.500	2.15
12	214.2	784		6.05	6.67	2.65	0.15	8.00	0.500	2.62
13	231.2	785		5.55	4.83	3.11	0.16	8.26	0.500	3.38
14	189.4	787		2.26	6.00	0.76	0.08	4.38	0.500	1.27
15	195.3	778		2.37	6.53	0.64	0.08	4.16	0.500	1.26
16	198.9	779		4.39	8.22	0.34	0.17	4.45	0.500	0.89
17	200.0	774		5.30	13.8	0.52	0.19	7.01	0.500	0.74

alcohol passing the catalyst per hour. Columns 12 and 13 give the initial ratio in molecules of ester to hydrogen, and are calculated (1) from the vapour pressure of the ester and the total pressure in the saturator, (2) from the analysis of the products; in the decomposition experiments the ratio should obviously be 0.500. These values give a check on the analyses, and show a satisfactory agreement. The values in the last column are those of the constant  $K_1 = C_{H_2}^2 C_{CH_3OCH} / C_{CH_3OH}^2$ .

The values of  $\log_{10} K_1$  (expts. 1—15) are plotted in Fig. 1 against  $1/T$ ; they show that the results of association and dissociation experiments lie on the same curve, proving that true equilibrium was reached. The values of  $K_2$  for the reaction  $CH_3 \cdot O \cdot OCH = CO + CH_3 \cdot OH$  were so discordant as to show that equilibrium had not

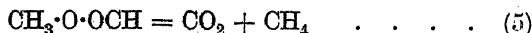
FIG. 1.



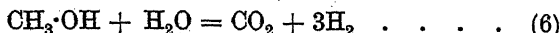
△ (dissociation) refers to experiments starting with  $CH_3 \cdot OH$  [reaction (-1)].  
 ○ (association) " " " " "  $H_2 + CH_3 \cdot O \cdot OCH$  [reaction (1)].

been reached. The values obtained from expt. 15 (Fig. 1) and expts. 16 and 17 (not plotted) lie well below the curve; evidently the catalyst, which was the same in all these experiments, had lost its activity, so that even the equilibrium ( $\pm 1$ ) was not now attained.

The values for  $CO_2$  and  $CH_4$  in the table suggest that the reaction



took place to a slight extent. If, however, a trace of water was present, carbon dioxide may have been formed by the reaction



(*J. Amer. Chem. Soc.*, 1921, 43, 1670); this would explain the excess of carbon dioxide found in some of the experiments.

The equilibrium constant of reaction (2) was determined in a

similar manner and in the same apparatus. The catalyst here was solid sodium methoxide. This absorbed some carbon monoxide, and hence the results are not very trustworthy. The same thing occurred, but to a much smaller extent (about 1 mol. of sodium methoxide disappearing for every 100 mols. of carbon monoxide converted into methyl formate), when the reaction was carried out in solution, and in this case the reaction causing the carbon monoxide to disappear was shown to be  $\text{CH}_3\cdot\text{O}\cdot\text{OCH} + \text{NaO}\cdot\text{CH}_3 = \text{CH}_3\cdot\text{O}\cdot\text{CH}_3 + \text{NaO}\cdot\text{OCH}$ . Hence the values of the equilibrium constant  $K_2$  are only to be regarded as preliminary, but those of the association and dissociation experiments agree fairly well, as the following table shows.

TABLE II.

Reaction.	Temp.	Log $K_2$ by exper.	Log $K_2$ calc.
(-2)	102°	1.82	1.81
(2)	74	1.53	1.40
(-2)	74	1.40	1.40
(-2)	70	1.29	1.34

$K_2 = C_{\text{CO}} \cdot C_{\text{CH}_3\cdot\text{OH}} / C_{\text{CH}_3\text{OOCCH}}$  is for the gas mixture leaving the catalyst. The values in column 4 are calculated by the equation  $\log_{10} K_2 = -1880/T + 4.82$ .

The effect of temperature on equilibrium should be accurately given over a fairly wide range by an expression of the form

$$\log_{10} K = -A/T + B,$$

where  $A$  = heat of reaction at constant volume divided by 4.571, and  $B$  is a constant (Scheffer, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, 19, 636). Values calculated on this formula are in Table II and are represented by the straight line in Fig. 1. The values given in the literature for the heats of combustion of methyl alcohol and methyl formate are discordant, Stohmann's value for methyl alcohol being about 2 Cals. lower than that of Thomsen. I have preferred to use the latter, since, although Thomsen's "universal burner" is apt to give somewhat high values, the error may be expected to be small when the substances are volatile, whilst, on the other hand, Stohmann's values, according to Roth (*Z. Elektrochem.*, 1911, 17, 789), may be suspected to be low, especially in the case of volatile liquids.

The heat capacity of methyl alcohol has been calculated from the values in Landolt-Börnstein's tables for the ratio,  $k$ , between the two heat capacities. For methyl formate, no direct data seem to be available, but from the value for ethyl formate and those for methyl and ethyl alcohols the heat capacity of methyl formate (at constant volume) has been estimated at 10 cals. per degree.

The following table contains all the numerical values used in the calculation of the reaction heats at the temperatures in question.

Substance.	Heat of combustion at const. press.	Heat capacity at const. vol.
Methyl alcohol .....	182,230	7.8
Methyl formate .....	241,210	10.0
Carbon monoxide .....	67,960	5.0
Hydrogen .....	68,430	4.8

By means of this table the heat of reaction (1) at constant volume and about 200° is calculated to be 13,800 cal. and that of reaction (2) at about 100°, 8,600 cal. From these values and the above determinations of the equilibrium constants, the constants,  $B$ , of reactions (1) and (2) can be calculated as 3.61 and 4.82, respectively. These two numbers thus contain the results of the above investigation of the two reactions.

It is now possible to obtain from Fig. 1 and Table II a preliminary value of the equilibrium constant  $K_3 = C_{\text{CO}} \cdot C_{\text{H}_2}^2 / C_{\text{CH}_3\text{OH}}$  for the reaction (3). Calculation shows that

$$\log K_3 = -4896/T + 8.43 \quad . \quad . \quad . \quad (7)$$

From (7) it can be calculated that at about 200°  $K_3$  is about  $10^{-2}$ , so that at this temperature, if the hydrogen concentration is 1 mol. per litre, only 1% of the carbon monoxide will remain if the reaction  $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$  proceeds until equilibrium has been reached, whilst, on the other hand, if the hydrogen concentration is 0.01, only 1% of the carbon monoxide will be transformed into methyl alcohol.

The value of  $K_3$  can also be roughly predicted by means of one of the well-known approximate equations arrived at from Nernst's third law of thermodynamics, for instance, the one given by Nernst himself,

$$\log K_p = -Q_{18}/4.57T + 3.5 \log T + 2i_{\text{H}_2} + i_{\text{CO}} - i_{\text{CH}_3\text{OH}} \quad (8)$$

where the  $i$ 's are the so-called conventional chemical constants of the different molecular species.

As shown by Cederberg (*Dissert.*, Upsala, 1916), a close connexion seems to exist between the critical pressure of a substance and its chemical constant and therefore I have used the values  $i_{\text{H}_2} = 1.6$ ;  $i_{\text{CO}} = i_{\text{N}_2} = 2.6$ ;  $i_{\text{CH}_3\text{OH}} = i_{\text{SO}_2} = 3.3$  (see Pollitzer, *Ahrens's Sammlung* 17, 1912).

By means of  $K_p = (RT)^2 K_c$  and the data just mentioned we thus find

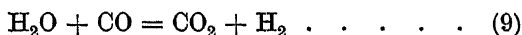
$$\log K_3 = -22700/4.57T + 1.5 \log T + 4.7 \quad . \quad . \quad (8, i)$$

As furthermore  $1.5 \log T$  at temperatures about 200° is very nearly equal to 4.0, the equation becomes

$$\log K_3 = -4966/T + 8.7 \quad . \quad . \quad . \quad (8, ii)$$

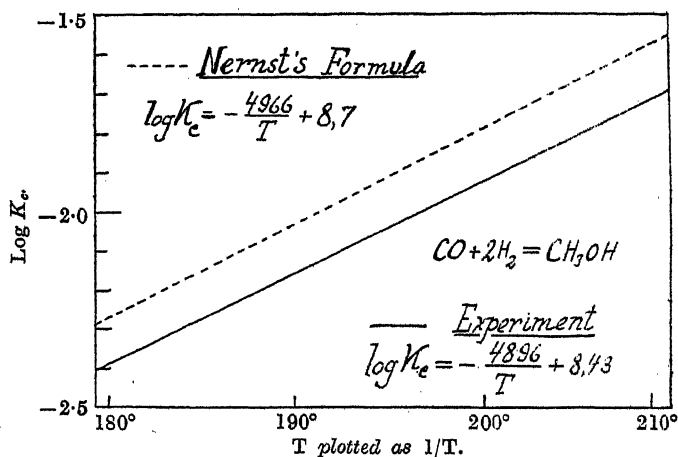
The agreement (see Fig. 2) between (8, ii) and (7) is as good as could be expected, considering the preliminary character of the investigation of reaction (2) and the approximations implied in the use of the Nernst equation (8).

By combining equation (7) with a similar relation derived from earlier experiments on the reaction



it is furthermore possible to calculate the equilibrium constant of the reaction (6). If we define  $K_9$  by means of the equation  $K_9 = C_{\text{H}_2\text{O}} \cdot C_{\text{CO}} / C_{\text{CO}_2} \cdot C_{\text{H}_2}$ , where the concentrations are those at equi-

FIG. 2.



librium, we get from Hahn's experiments (*Z. physikal. Chem.*, 1903, 44, 513; 1904, 48, 735; see Haber, "Thermodynamik technischer Gasreaktionen," Berlin, 1905)

$$\log_{10} K_9 = -1854/T + 1.66 \quad (10)$$

When this equation is subtracted from (8, ii) we obtain

$$\log_{10} K_6 = -3042/T + 6.77 \quad (11)$$

where  $K_6$  is the equilibrium value of  $C_{\text{CO}_2} \cdot C_{\text{H}_2}^2 / C_{\text{CH}_3\text{OH}} \cdot C_{\text{H}_2\text{O}}$ .

Finally it should be remarked that by means of existing data on the equilibria



and



and the equations given above, it should also be possible to calculate the value of the equilibrium constant for the reaction (5).

The first of these reactions has been investigated by Mayer and

Altmayer (*Ber.*, 1907, **40**, 2134), Coward and Wilson (*J.*, 1919, **115**, 1380), and Pring and Fairlie (*J.*, 1912, **101**, 91). The results of these authors may be represented with sufficient accuracy by means of the equation

$$\log K_p = \log \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} = \frac{5450}{T} - 6.33 \quad . \quad . \quad (14)$$

If we wish to get  $K_c = C_{\text{CH}_4}/C_{\text{H}_2}^2$  with the concentrations expressed in mols. per litre, we must add  $\log RT = \log T - 1.09$  and consequently

$$\log K_c = 5450/T + \log T - 7.42 \quad . \quad . \quad (14, i)$$

For the reaction (14) a summary of the existing data is to be found in a paper by Jellinek and Diethelm (*Z. anorg. Chem.*, 1922, **124**, 220). From their table of the mean values of  $K_p$  found at different temperatures by different authors, the following expression may be calculated :

$$\log K_p = 8620/T - 8.80 \quad . \quad . \quad (15)$$

and transforming into  $K_c$ ,

$$\log K_c = \log \frac{C_{\text{CO}_2}}{C_{\text{CO}}^2} = \frac{8620}{T} + \log T - 9.89 \quad . \quad (15, i)$$

By adding these equations we get the equilibrium constant for the reaction  $2\text{H}_2 + 2\text{CO} = \text{CH}_4 + \text{CO}_2$ , viz.,

$$\log K_p = \log \frac{p_{\text{CH}_4} \cdot p_{\text{CO}_2}}{p_{\text{H}_2}^2 \cdot p_{\text{CO}}^2} = \frac{14070}{T} - 15.13 \quad . \quad . \quad (16)$$

$$\text{or} \quad \log K_c = \log \frac{C_{\text{CH}_4} \cdot C_{\text{CO}_2}}{C_{\text{H}_2}^2 \cdot C_{\text{CO}}^2} = \frac{14070}{T} + 2 \log T - 17.31 \quad (16, i)$$

Adding to this the equation (7), we get the logarithm of the equilibrium constant for the reaction  $\text{CH}_3\text{-OH} + \text{CO} = \text{CH}_4 + \text{CO}_2$ , viz.,

$$\log K_c = \log \frac{C_{\text{CH}_4} \cdot C_{\text{CO}_2}}{C_{\text{CH}_3\text{-OH}} \cdot C_{\text{CO}}} = \frac{9170}{T} + 2 \log T - 8.88 \quad . \quad (17)$$

from which it is evident that the formation of methyl alcohol from methane and carbon dioxide will take place only at temperatures at which methane is not at all stable, whilst it is possible, according to equations (11) and (7), to obtain reasonable amounts of methyl alcohol from hydrogen and either carbon monoxide or dioxide at not too high temperatures.

It is obvious that the equations given above all contain the uncertainty introduced by the use of the preliminary results for the equilibrium between carbon monoxide, methyl alcohol, and methyl formate.



*Summary.*

(1) The equilibrium constant of the reaction  $\text{CH}_3\cdot\text{O}\cdot\text{OCH} + 2\text{H}_2 = 2\text{CH}_3\cdot\text{OH}$  has been determined with fair accuracy at temperatures in the neighbourhood of  $200^\circ$ .

(2) Preliminary values for the equilibrium constant of the reaction  $\text{CH}_3\cdot\text{OH} + \text{CO} = \text{CH}_3\cdot\text{O}\cdot\text{OCH}$  at about  $100^\circ$  have been given.

(3) It is shown that by combination of the found values with existing data the equilibrium constants of the reactions  $\text{CO} + 2\text{H}_2 = \text{CH}_3\cdot\text{OH}$ ;  $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\cdot\text{OH} + \text{H}_2\text{O}$ ; and  $\text{CH}_4 + \text{CO}_2 = \text{CH}_3\cdot\text{OH} + \text{CO}$  may be calculated.

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[Received, September 21st, 1925.]

# LV.—*The Equilibria underlying the Soap-boiling Processes. The System Potassium Oleate–Potassium Chloride–Water.*

By JAMES WILLIAM MCBAIN and WILLIAM JOSEPH ELFORD.

THE study of soap solutions has shown that they exist in a number of forms, each with very striking characteristics. In pursuing the systematic study of the constitution of these liquids, jellies, liquid crystals, and curds, it is essential that the conditions under which each exists should be exactly delimited. Further, the processes of soap-boiling depend on the existence of this series of well-defined equilibria, which have, however, received very little systematic study.

We are now in a position to state that all soaps, pure, mixed commercial, whether potassium or sodium, are essentially of the same type. The differences are in degree and not in kind and the equilibria are so similar in the various cases that by means of numerical factors the effect of any electrolyte or mixture of electrolytes can be fairly closely predicted. Finally, to a large extent, the behaviour of a mixture of soaps can be inferred from that of its pure constituents taken separately. It is found also that the results from such small-scale laboratory experiments as are described in the present paper are in numerical agreement with similar results obtained on a full commercial scale.

Two previous contributions (McBain and Burnett, J., 1922, 121, 1320; McBain and Langdon, J., 1925, 127, 852) have dealt with the preliminary studies of sodium laurate and sodium palmitate in which the chief results were to show the various kinds of soap systems which exist, and to indicate some of the limits for the existence of ordinary isotropic soap solutions. The present instal-

ment is an account of a more thorough study of systems derived from potassium oleate,\* which possesses the advantage of being so soluble that all the possible systems can be observed at room temperature. Further, application of the new methods of optical investigation that were developed in a previous study of potassium laurate have enabled progress to be made with the delimitation of the two important anisotropic liquids, neat soap and middle soap.

All these phases exist equally well in the absence of salt and the simplest procedure is to begin with the two-component system oleate and water, in which most of the typical equilibria appear. Accordingly, this will be discussed first, together with observations made upon individual phases, followed by the data obtained with systems in which potassium oleate is the third component.

*Materials.*—Kahlbaum's ordinary potassium oleate was found to be unsuitable, as it was not homogeneous and contained excess of acid and not only did the concentrated solutions on warming become dark reddish-brown but they sometimes differed in physical state from those of purer potassium oleate. Our preparations were therefore made by neutralising oleic acid "Kahlbaum" with potassium ethoxide and when carefully dried remained as white powders. The oleic acid in each case had a nearly correct iodine value and a molecular weight (by titration) about 1% too high (compare Laing and McBain, J., 1920, 117, 1506). Potassium chloride "Kahlbaum" was used. Solutions were prepared in sealed thick-walled tubes of Duro glass by weighing in the requisite quantities and heating to whatever temperature was necessary to transform the contents into a single homogeneous liquid. Heating up to 170° was best carried out in a bath of glycerol, but for heating aqueous solutions to temperatures up to 400° an electric oven with mica windows was used and care was taken to heat and cool very slowly in order that adequate time should be allowed for the soap system to acquire the successive temperatures. Stirring was effected by slowly shaking the furnace as a whole, formation of air bubbles being avoided. In some cases a bath of the eutectic mixture of the nitrates of sodium and potassium was employed.

*Methods of Observation.*—In every soap system it is possible to observe a temperature,  $T_i$ , on heating to which it becomes a single homogeneous, isotropic liquid. For example, pure dry potassium oleate melts at 235–240° to form liquid crystal which, as will be shown, represents a point in the neat soap field, but on further

\* A preliminary study was carried out by F. T. Maggs, who determined a number of points on the boundaries of the region of isotropic soap solutions.

heating to  $300^{\circ}$  this melts sharply to form an ordinary clear isotropic liquid. This liquid is miscible with water in all proportions; the more water present, in general the lower the temperature  $T_i$ , and at room temperature potassium oleate solutions up to  $0.7N_w$  are clear and isotropic.

All subsequent experience has confirmed the observations of McBain and Burnett (*loc. cit.*) that no supersaturation occurs, with respect to formation of anisotropic liquid, upon cooling the isotropic solution, but supersaturation readily occurs with respect to formation of either true lamellar crystals or crystalline curd fibres or needles. The sudden change in viscosity which occurs when anisotropic liquid appears, and the even more sudden change accompanying the completion of its formation upon cooling sufficiently, serve as useful although very rough checks upon the optical observations.

We have found it essential to use polarised light both for macroscopic and for microscopic observation. It is possible to examine a number of systems at room temperature and up to  $80^{\circ}$ , using an ordinary object slide and cover glass and a Guttman heater (see MacLennan, *J. Soc. Chem. Ind.*, 1923, 42, 393T), but it is essential that a truly representative sample should be taken and that the whole of the sample be examined. It is necessary also to ensure that the conditions observed in the calibration of the temperature scale be maintained throughout. When a mixture of isotropic and anisotropic soap solutions is thinly spread out and thus examined between crossed Nicols, the dark isotropic patches are seen to be sharply differentiated from the illuminated anisotropic portions of the field.

For work at higher temperatures no suitable substance could be found for sealing the cover glass to the object slide, as in some cases the properties of the soap were much affected by it as well as by evaporation. Professor Kenrick of Toronto University kindly supplied a cell, made by fusing together two optically ground plates of pyrex glass, with narrow side tubes sealed in, and such a cell has been used up to  $120^{\circ}$ . Latterly we have used small flattened glass cells made from tubing, 2.5 mm. in diameter, blown into a small bulb which during the process of blowing is squeezed flat between two hot carbon blocks, leaving room for only a thin film therein. The cell could be filled with a representative sample by suction and then sealed off. Such cells were very readily annealed, any optical evidence of strain being thus removed. They could be employed in a small electric furnace on the stand of the microscope, and the temperatures there observed agree closely with those obtained by a macroscopic study of large tubes.

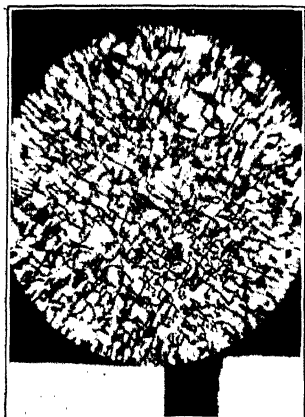
*Equilibria in the System Water-Potassium Oleate.*

Dilute aqueous potassium oleate is a homogeneous isotropic liquid which freezes with separation of ice, and at temperatures above  $300^{\circ}$  may without losing homogeneity be concentrated to 100% potassium oleate in the isotropic liquid condition. At all lower temperatures, potassium oleate is not miscible with water, but other intermediate phases are successively formed. Thus at  $20^{\circ}$  the highest concentration at which a homogeneous isotropic solution of potassium oleate can be prepared is  $0.70N_w$  (g.-mol. per 1000 g. of water). Above this concentration, an upper layer of higher concentration separates. This phase is a conic, anisotropic liquid and has been called in this laboratory "middle soap" (*Nature*, 1924, 113, 534; 114, 49; *Science*, 1925, 61, 613; McBain and Langdon, *loc. cit.*). Middle soap exists over a limited range of concentrations as a homogeneous phase which constitutes, like the isotropic solutions, a colloidal electrolyte. There is no great difference in molar conductivity between soap in the middle soap phase and soap in the isotropic phase. Middle soap up to  $1.25N_w$  shows no structure in the cardiod ultramicroscope, but above this concentration diffuse granular patches begin to show against the dark background.

Middle soap exists over only a limited range of concentrations, above which another distinct phase of still more concentrated solution appears. To this phase we have extended the term "neat soap." Neat soap resembles middle soap in being a conic anisotropic liquid and in being plastic; that is, devoid of noticeable elasticity. Each is rigid, the neat soap much less so with about the consistency of vaselin. Middle soap is darker than neat soap (due to presence of impurity). A moderately thin specimen of middle soap is clear and transparent, whereas neat soap is better described as semi-transparent and somewhat turbid. The heterogeneous mixture of these two is rigid and turbid, the turbidity being at a maximum between the normalities  $5N_w$  and  $6N_w$ . The exact range of concentrations for the existence of these phases has still to be determined, but for middle soap it lies between about  $0.9N_w$  and  $3.4N_w$  and for neat soap between  $7.5N_w$  and  $12N_w$ , within which limits a uniform field is obtained (see photograph I).

In many of the otherwise clear systems described above, small, white, star-like growths develop with time. Examination in the ultramicroscope shows them to consist of small rods plaited together to form branching structures. They probably consist of acid soaps produced by hydrolysis.

Photograph I, of  $9N_w$ -potassium oleate in polarised light, shows that neat soap, like middle soap, is a homogeneous, conic, anisotropic liquid soap with uniaxial interference figures. Further, on



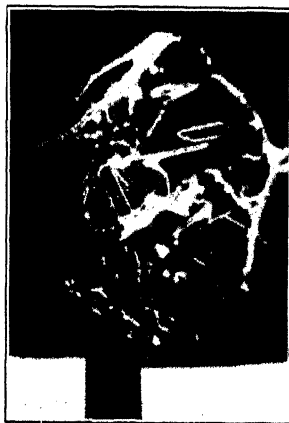
I.— $9N_w$  Potassium oleate at room temperature. Crossed nicols.  $\times 250$ .



II.—Concentrated aqueous potassium oleate. Crystal phase. Crossed nicols.  $\times 250$ .



III.— $25N_w$  Potassium oleate at room temperature. Showing crystalline flakes and anisotropic fluid. Crossed nicols.  $\times 60$ .



IV.— $13.3N_w$  Potassium oleate at room temperature. Crystals as seen under cardiod ultramicroscope.



cooling  $4N_w$ -potassium oleate below its critical temperature,  $T_c$  240°, the drops of neat soap which begin to appear separate in the form of the double cones which Lehmann (*Weid. Ann.*, 1895, 56, 771, etc.) gave as a classical illustration of liquid crystals in systems containing ammonium oleate. Ethyl azoxybenzoate likewise separates in the form of these double cones when cooled from the isotropic, amorphous liquid condition. Friedel (*Ann. Physique*, 1922, 18, 273) terms this structure "batomet" and regards it as proof that such systems are to be included in his so-called "smectic" group. Evidently both neat soap and middle soap are anisotropic liquids which would be included in the smectic group, and no soap systems are yet known which could be classified as "nematic." The fact that curd fibres have been shown by Mr. S. H. Piper to give radiograms with lines corresponding to spacings in three dimensions is a positive disproof of Friedel's contention that they were to be included in his "smectic" group, although he renamed the "liquides à conique" (conic anisotropic liquids) specially to include them.

At temperatures between 240° and 300° neat soap may be concentrated up to 100% anhydrous potassium oleate, but at lower temperatures there is an upper limit fixed by the separation of crystalline potassium oleate, usually in the form of extremely thin, hexagonal flakes. In the  $50N_w$ -solution there is still some neat soap left, showing that the hydration of the crystals cannot exceed 1 mol. of water per mol. of soap. It is not known whether these crystals of slightly hydrated potassium oleate can be dehydrated to anhydrous potassium oleate without any new phase separating. The excessively thin crystal plates are readily bent and are illustrated in photograph II.

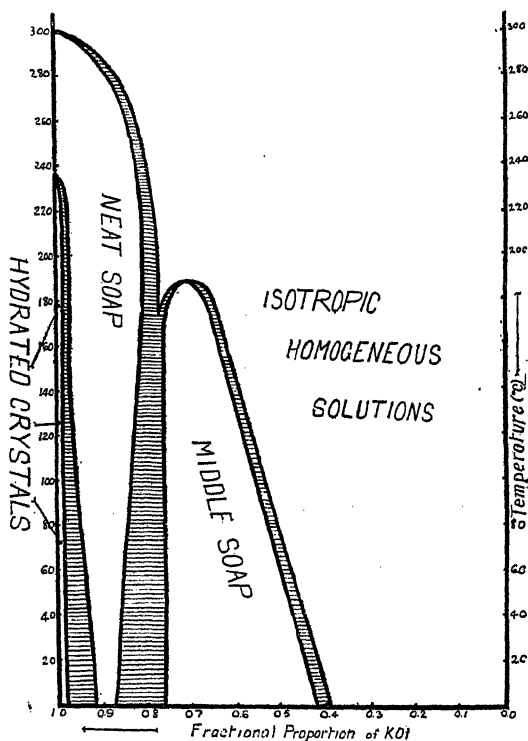
The sharply outlined hexagonal lamellæ are sometimes thin enough to give interference colours in ordinary light, and under a polarising microscope exhibit polarisation colours and give sharp uniform extinction in four positions. A mass of the crystals has a wax-like consistency and presents a silvery appearance. Photographs III and IV show these crystals mixed with neat soap in the heterogeneous systems.

Thus in passing from one pure component, water, to the other pure component, potassium oleate, at 20°, at least four different phases are met with and the solutions are alternately homogeneous and heterogeneous. At temperatures above 180°, the very remarkable behaviour is met with that there is a region of homogeneous isotropic phase above the middle soap as well as below it, so that, for example, at 177°, on steadily concentrating an isotropic solution the anisotropic middle soap separates, and after its formation is completed and the solution is slightly more concentrated, isotropic

solution of still higher concentration begins to appear but exists over a narrow range, whereupon neat soap appears.

All these relations are shown in Fig. 1 and some of the numerical data from which the figure has been plotted are in Tables IA, B, C and D. The temperatures there recorded are  $T_i$ , the minimum temperature at which the system is a homogeneous isotropic liquid,

FIG. 1.



*Equilibrium diagram for the two-component system water-potassium oleate, showing the stable, homogeneous phases that occur at various temperatures. The boundary of the isotropic solution only is accurately known.*

determined visually or with the aid of optical apparatus;  $T_h$ , the temperature on heating to which anisotropic plastic liquid shows, by a marked fall in rigidity, that isotropic liquid is beginning to separate; and  $T_c$ , the temperature on heating to which crystals just disappear to form homogeneous neat soap. Concentrations are expressed in weight normality ( $N_w$ ), and also in "fractional proportions" of potassium oleate,  $N_w/(N_w + 1)$ , for use later in the triangular diagram of the three-component system.



TABLE IA.

*Appearance of aqueous potassium oleate at room temperature and phases present, together with temperatures,  $T_i$ , on heating to which the system becomes a clear homogeneous liquid.*

*Series a. Tubes partly evacuated before sealing.\**

System ( $N_w$ ).	Fractional proportion of K oleate.	Description of material at room temp.	$T_i$ (visual).
0.70	0.412	Viscous, colourless, isotropic liquid.	12°
0.72	0.419	Hetero. M. soap and isotropic liquid.	22
0.75	0.429	Hetero., etc., very viscous.	33
0.78	0.438	Clear, firm M. soap.	42
1.00	0.500	Clear, rigid M. soap, yellowish-brown.	72
1.50	0.600		138
2.00	0.667	Clear, rigid, M. soap, deep colour.	185
2.50	0.714	" " "	173
3.00	0.750	Hetero.†	175
3.50	0.778	Hetero.‡	184

Homo. = homogeneous. Hetero. = heterogeneous. M. soap = "middle soap." N. soap = "neat soap."

\* The above systems were prepared from oleic acid of mol. wt. 285 and were all more deeply coloured than those prepared with 1924 (B) and 1925 soaps, possibly owing to a very slight amount of free oleic acid, which becomes oxidised at high temperatures. This would provide a possible explanation of the marked difference between 3.5 $N_w$ -solution prepared with this sample of soap and that prepared with succeeding samples.

† Minute droplets of a lemon-white phase in a brownish-red phase; system still rigid and plastic.

‡ Two immiscible plastic fluids, one lemon-coloured and tending to accumulate at the surface, the other deep reddish-brown and accumulating at the bottom of the tube.

TABLE IB.

*Tubes not evacuated.\**

System ( $N_w$ ).	Fractional proportion of K oleate.	Description of material at room temp. (18—20°).	$T_i$ (visual).
0.80	0.444	Hetero. M. soap and isotropic liquid.	34.5°
0.85	0.458	Homo. clear firm M. soap.	57
0.91	0.476	" " "	67
1.25	0.556	" " "	118
2.00	0.667	" " "	183.5
2.50	0.714	" " "	188
2.75	0.733	" " "	188-15
2.98	0.748	" " "	186
3.20	0.762	" " "	185
3.50	0.778†	" " "	200
4.00	0.800	Rigid, anisotropic, definitely turbid.	237.5

\* Prepared from oleic acid of mol. wt. 286.

† Not quite as transparent as the 3.2 $N_w$ -solution.

TABLE IC.

*Tubes not evacuated.\**

System ( $N_w$ ).	Fractional proportion of K oleate.	Description of material at room temp. (18–20°).	$T_i$ (visual).	$T_1$ (opt.).	$T_c$ (visual).	$T_h$ (opt.).
0-80	0-444	Viscous, hetero. M soap and isotropic liquid.	31.5°	32.5°.	—	—
1-00	0-500	Clear, rigid M. soap.	72	76	—	55°
1-50	0-600	" " "	139	142.5	—	127
1-75	0-636	" " "	161	173	—	163
2-00	0-667	" " "	180	184	—	174
2-50	0-714	" " "	188	—	—	—
2-75	0-733	" " "	190	187.5	—	187
3-00	0-750	" " "	185.5	—	—	—
3-10	0-756	" " "	184.5	185.5	—	181
3-20	0-762	" " "	183	—	—	—
3-28	0-766	" " "	179.5	—	—	—
3-40	0-773	" " "	178.5	—	—	—
3-50	0-778†	" " "	194.5	200.5	—	173
4-00	0-800	Rigid, turbid N. soap and M. soap.	235.5	242	—	—
5-00	0-833	Hetero. rigid N. soap and M. soap.	261	—	—	—
6-00	0-857	Firm, hetero. N. soap and M. soap.	274.5	—	—	—
7-00	0-875	Semi-transparent N. soap.‡	283	—	—	—
8-00	0-889	Semi-transparent N. soap.§	280	—	—	—
9-00	0-900	Soft, semi-transparent N. soap.	287	—	—	—
10-00	—	" " "	288.5	—	—	—
12-00	0-923	" " "	291	—	26°	—
15-00	0-937	Hetero. N soap and cryst. flakes.	291.5	—	55	—
25-00	0-962	" " "	293	—	98	—
30-00	0-968	" " "	291	—	118	—
40-00	0-975	" " "	303	—	132	—
50-00	0-980	" " "	305	—	150	—

\* Prepared from oleic acid of mol. wt. 286.

† Reproduction of 1924 (B).

‡ Turbidity subdued, and consistency less firm; can just be displaced by shaking.

§ Fluid, soft and non-homogeneous in appearance.

TABLE ID.

*Systems prepared from pure aqueous potassium hydroxide and  
Kahlbaum's oleic acid, mol. wt. 285.*

System ( $N_w$ ).	Fractional proportion of K oleate.	Description of material at room temp. (18–20°).	$T_i$ (visual).
1-15	0-535	Rigid M soap.	93.0°
1-24	0-552	" "	115

*Effect of the Presence of Potassium Chloride in Isotropic Solutions  
of Potassium Oleate.*

Qualitative observations have been described by M. H. Fischer  
("Soaps and Proteins," New York, 1921) on the effect of adding

salts to ordinary soap solutions. Some of his experiments were repeated by Miss King (*J. Soc. Chem. Ind.*, 1922, 41, 147T). Fischer's observations were confined to fairly dilute soap solutions and were evidently influenced by the difficulties of ensuring adequate mixing and avoiding oxidation of soap, which greatly affect the results. The following observations were made by Miss King and F. T. Maggs as well as by ourselves.

The most important effect is that, whilst moderate additions of such salts as potassium chloride and potassium thiocyanate progressively increase the viscosity of the liquid, there is an ill-defined range of concentrations of salt for which the potassium oleate solutions set to a clear, transparent, elastic jelly like table jelly. For potassium chloride and potassium thiocyanate these concentrations are between about 0.4 and  $0.8N_w$ . This range is somewhat wider if sufficient time is given for gelatinisation; the whole system remaining homogeneous and clear if hydrolysis and oxidation are avoided.

Still further small additions of salt reduce the jelly to a more or less viscous, homogeneous liquid. In solutions of such soaps as do not gelatinise under the given conditions, for example, sodium palmitate at  $81^\circ$ , the viscosity rises to a maximum and then falls off very greatly before any salting-out takes place (compare Miss King's graph, *loc. cit.*). Similar behaviour is observed within the whole range of isotropic solutions.

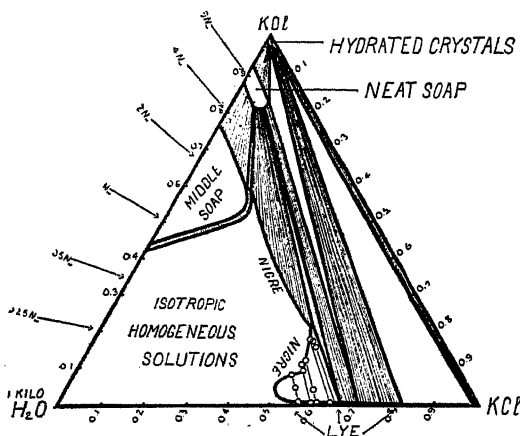
Still higher concentrations of salt cause separation of the soap solution into two layers. The concentration of salt necessary to effect this depends, in a rather complicated way, on the concentration of the soap, as is seen in Figs. 2, etc., in which the boundaries of the isotropic field are accurately mapped. If the solutions are sufficiently dilute, say below  $0.6N_w$ -potassium oleate, the two liquid layers formed are both isotropic and are represented on the diagram within an indentation in the isotropic liquid boundary. The upper layer is "nigre" and contains most of the soap; the lower layer is "lye" containing a minute concentration of soap and a concentration of salt slightly higher than that in the nigre.

If the soap solution is more concentrated, say between  $0.75N_w$  and  $3N_w$ , the two phases separating out are neat soap and nigre. It will be noted that the presence of the salt greatly increases the possible concentration of soap in the isotropic solution; thus at  $20^\circ$  in the absence of salt the highest concentration at which potassium oleate forms a homogeneous isotropic liquid is  $0.70N_w$ , whereas in the presence of  $0.176N_w$ -potassium chloride the concentration of the soap may be increased to  $3N_w$ . As in the two-component system, so in the three-component system, increasing temperature extends the boundaries of the isotropic field.

*Equilibria in the System Water-Potassium Oleate-Potassium Chloride.*

Middle soap and neat soap, like isotropic solution, extend from the two-component system, aqueous potassium oleate, into the three-component system; thus not only is the two-component system the limiting boundary of the three-component system, but the same phases occur in each and no new ones appear through addition of salt. Discussion of the three-component system is thus reduced to delimiting the boundaries for the existence of the phases, the appearance and properties of which have previously been dealt with. In other words, a reference to the foregoing discussion of

FIG. 2.



Phase rule diagram at 20°. Potassium oleate-potassium chloride-water; concentrations being expressed in fractions of mols. of potassium oleate and potassium chloride, but in fractions of one kilogram of water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

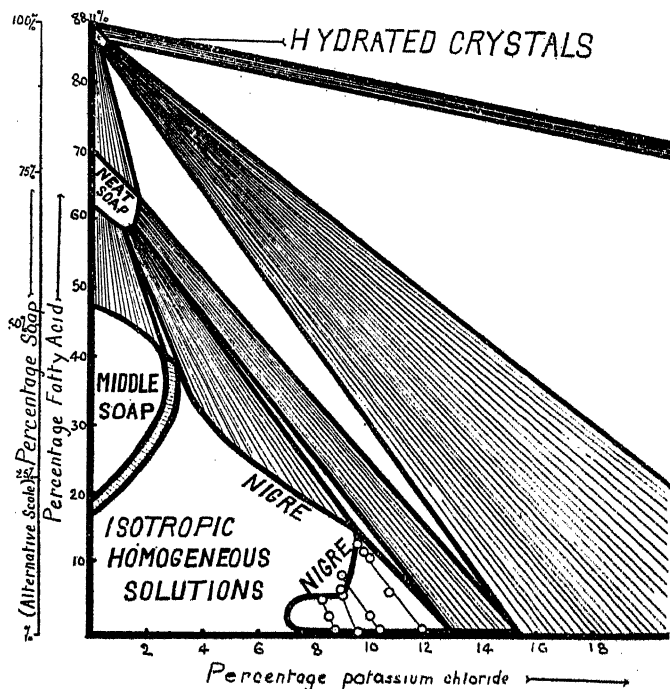
the two-component systems shows that solutions of pure soap spontaneously "salt out" in the absence of salt.

Most of the observations consisted in noting carefully the temperatures,  $T_i$ , at which heterogeneous systems just became isotropic, and it was found that these homogeneous isotropic solutions separated again at the same temperatures on cooling. It is only when the true crystalline lamellæ are due to appear that supersaturation has ever been observed.

Addition of salt to middle soap lowers the temperature,  $T_i$ , at which it becomes isotropic. Likewise, at higher temperatures, its field of existence progressively diminishes until at 189° it is reduced to a single point in the two-component system.

In most cases separation of the phases was so imperfect that they remained permanently in intimate mixture as a rigid, or extremely viscous mass, so that samples could not be separated for analysis. Indeed, the complete separation of neat soap from nigre, even in full-scale commercial work, is an art which calls for the highest skill on the part of the soap boiler, and middle soap has never been studied on the commercial scale. Apart from the extremely ready

FIG. 3.



Phase rule diagram at 20°, potassium oleate-potassium chloride-water; concentrations being expressed in grams of fatty anhydride and grams of potassium chloride per 100 grams of total system. The areas correspond to those in Fig. 2.

separation of lye from nigre, it has been considered impossible to effect separations in small-scale experiments. However, recent experience indicates that at high temperatures certain of these separations may be possible which will then permit of direct analyses of the separated layers.

The data are in Table II and the isotherms deduced therefrom are shown in Figs. 2 to 5, which should be compared with the corresponding diagrams for sodium palmitate (McBain and

Langdon, *loc. cit.*), where also a fuller introduction to the subject is given.

The five tie-lines between nigre and lye shown in Figs. 2 and 3, which illustrate the general equilibria at 20°, were obtained by direct analyses of the two phases in equilibrium with each other. The cross in the middle of each line represents the total composition of each system which should, of course, lie upon the straight line connecting the compositions of the two phases in each case.

TABLE II.

*Effect of addition of potassium chloride to 0.1N<sub>w</sub>-potassium oleate; appearance and phases present at room temperature, and T<sub>1</sub> the temperature on heating to which the system becomes a clear homogeneous liquid.*

Conc. of KCl (N <sub>w</sub> ).	Description of material at room temp. (18°).	T <sub>1</sub> (visual).
0.00	Homo. transparent, isotropic liquid.	—
0.5	Isotropic, colourless, jelly-like system.	—
1.0	Moderately viscous, isotropic, opalescent liquid.	—
1.05	Two liquid layers; nigre and lye.*	25°
1.20	" " " " Both isotropic.	119
1.30	" " " " " "	127
1.50	" " " " " "	156
1.80	Two layers, upper hetero.	185
2.0	Two layers, N. soap and lye.	205

\* Upper layer the more viscous, lower limpid lye, both isotropic.

*Effect of addition to 0.25N<sub>w</sub>-solutions of potassium oleate.*

0.25	Colourless, limpid liquid, isotropic.	—
0.50	Clear, viscous liquid, isotropic.	—
1.00	Clear, very viscous, isotropic liquid.	—
1.25	Clear, isotropic, viscous liquid.	—
1.50	Two liquid layers, both isotropic.	100
1.65	" " " " " "	159
2.0	Two layers, upper hetero., lower lye	184
2.2	Two layers, upper viscous, lower lye.	204

*Effect of addition to 0.50N<sub>w</sub>-solutions of potassium oleate.*

0.00	Clear, transparent, isotropic, mobile liquid.	—
0.25	Clear, isotropic, very viscous liquid.	—
0.50	Transparent, isotropic, elastic jelly.	—
1.00	Clear, viscous, isotropic liquid.	—
1.65	Two liquid layers, both isotropic.	75
1.67	" " " " " "	124
1.70	" " " " " "	120
1.80	Two layers, upper creamy, lower lye.	167
2.0	" " " " " " Lye increasing.	178
2.3	Two layers, N. soap and lye.	207

*Effect of addition to 0.75N<sub>w</sub>-solutions of potassium oleate.*

Conc. of KCl (N <sub>w</sub> ).	Description of material at room temp. (18°)	T <sub>i</sub> (visual).
0.00	Hetero. M. soap and isotropic liquid.	33
0.1	Clear, elastic jelly, isotropic.*	—
0.25	Clear, transparent, elastic jelly, isotropic.*	—
0.50	Clear, transparent, rigid jelly, isotropic.	—
1.0	Clear, transparent jelly, isotropic.*	—
1.5	Clear, viscous, isotropic liquid.	—
1.7	Viscous hetero. system.†	25
1.75	Hetero.; bad separation.‡	109
1.85	Hetero., three liquid phases.§	150
2.0	Viscous, turbid, upper layer.	158
2.3	Turbid, aniso. upper layer and lye.	195
2.5	" " " "	206
2.75	" " " "	229.5

\* Not perfectly rigid.

† Small amount of anisotropic phase at surface.

‡ Mainly clear, isotropic liquid of moderate viscosity; anisotropic phase near surface.

§ Middle nigre layer forms main bulk.

|| Lye growing at expense of nigre.

*Effect of addition to 1.0N<sub>w</sub>-solutions of potassium oleate.*

0.00	Aniso. plastic fluid, rigid.	72
0.085	" " " "	65
0.10	Aniso. fluid, possessing elasticity.	60
0.17	Hetero. aniso. phase and isotropic jelly.	30
0.25	Clear, isotropic, transparent jelly.	—
0.50	" " " "	—
1.00	Clear, viscous, isotropic liquid.	—
1.50	Viscous hetero. system.*	65
1.6	Viscous hetero. system.*	104.5
1.75	Viscous hetero. system, aniso. phase and nigre.	130
2.0	Two layers, upper turbid, lower lye.	156
2.5	Two layers, upper turbid and viscous, lower lye.	193
2.8	" " " " " "	212.5

\* Anisotropic phase tending to accumulate at the surface and viscous, isotropic liquid as lower layer; bad separation.

*Effect of addition to 1.5N<sub>w</sub>-solutions of potassium oleate.*

0.00	Aniso. plastic fluid, rigid.	138
0.2	" " " "	129.5
0.40	" " " "	90
0.46	Clear, very viscous, isotropic liquid.	—
1.0	Hetero. system.*	60
1.35	Hetero., viscous, aniso. phase and nigre.	129
1.50	" " " "	136
1.78	Two layers, upper hetero., lower lye.†	160
2.0	Two layers, upper turbid and viscous.	163
2.3	Two layers, upper turbid, lower lye.	191
2.5	Two layers, upper viscous and turbid, lower lye.	205

\* Small amount of anisotropic phase near surface, mainly viscous, isotropic liquid.

† Upper layer forms main portion.

*Note.*—Only results obtained with systems prepared in non-evacuated tubes are recorded in this and the following sections, i.e., results are those with 1924 (B) soap.

*Effect of addition to 2.0N<sub>w</sub>-solutions of potassium oleate.*

0.00	Clear, aniso., plastic fluid, rigid.	183.5
0.1	Aniso., plastic fluid, rigid.	178.5
0.2	" " "	167
0.3	" " "	159
0.4	" " "	153
0.5	" " less rigid.	136
0.6	Aniso. plastic fluid.	91
0.7	Mainly clear, isotropic jelly.*	—
0.8	Clear, viscous, isotropic liquid.	—
1.0	Hetero.; bad separation.†	110.5
1.2	" " "	143
1.3	" " "	154
1.5	" " "	160
1.65	Two layers, upper viscous and turbid, lower lye.	183
2.0	" " " " " "	—
2.2	" " " " " "	—

\* Little anisotropic phase near surface.

† Anisotropic phase and viscous, isotropic solution.

*Effect of addition to 2.5N<sub>w</sub>-solutions of potassium oleate.*

0.0	Aniso. plastic fluid.	188
0.1	" " "	186
0.2	" " "	179
0.3	" " "	166
0.4	" " "	154
0.5	" " "	108
0.6	Heterogeneous.*	86
0.7	Heterogeneous.*	121
0.79 †	Hetero. aniso. phase and nigre; bad separation.	142
1.0	" " " " " "	163
1.3	" " " " " "	188
1.5	Three phases, lye just appearing.	197.5
1.65	Two layers, viscous turbid layer and lye.	215
3.5	" " " " " "	247

\* Anisotropic phase near surface, mainly clear, viscous nigre.

† 0.79N<sub>w</sub>-KCl with 2.47N<sub>w</sub>-K oleate.

*Effect of addition to 2.75N<sub>w</sub>-solutions of potassium oleate.*

0.0	Aniso. plastic fluid, rigid.	188.5
0.2	" " "	170
0.25	" " "	164
0.30	" " "	158
0.40	" " "	144.8
0.50	Turbid, aniso., plastic fluid.	125
0.60	Hetero. aniso. phase and clear, viscous nigre.	150.5
0.80	" " " " " "	175
1.0	" " " " " "	184
1.65	Two layers, upper turbid and viscous, lower lye.	217



*Effect of addition to 3.0N<sub>w</sub>-solutions of potassium oleate.*

Conc. of KCl (N <sub>w</sub> ).	Description of material at room temp. (18°).	T <sub>i</sub> (visual).
0.0	Aniso. plastic fluid.	186
0.1	" " "	172
0.2	" " "	168
0.3	" " "	156
0.4	" " " Slight turbidity.	158
0.5	Viscous, semi-transparent system.	176
1.0	" " "	208
2.19	Turbid fluid, upper layer and lye.	—
3.0	" " " "	237.5

*Effect of addition to 3.5N<sub>w</sub>-solutions of potassium oleate.*

0.0	Aniso. plastic fluid.*	200
0.15	" " " Quite firm.	210.5
0.20	" " " "	216.5
0.40	" " " " "	224.5
0.50	" " " " "	228.0

\* Rigid but tending to turbidity.

*Effect of addition to 4.0N<sub>w</sub>-solutions of potassium oleate.*

0.0	Rigid, aniso., plastic fluid.*	237.5
0.5	" " " Turbid.	240
1.1	Two layers, neat soap and nigre.†	238

\* Definitely turbid.

† Good separation of brown nigre, forming about  $\frac{1}{2}$  of system.*Effect of addition to 5.0N<sub>w</sub>-solutions of potassium oleate.*

0.0	Very turbid, aniso., plastic fluid, rigid.	261
1.0	Two layers, N. soap and nigre.*	260

\* Good separation of brown nigre,  $\frac{1}{2}$  of system.

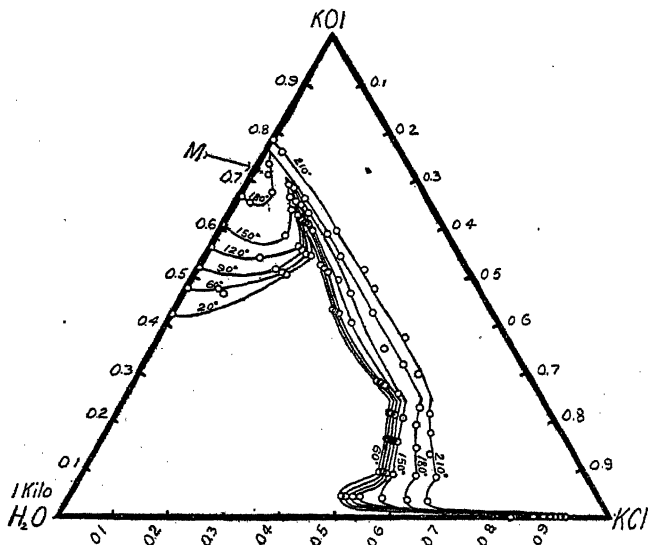
Fig. 2 represents the equilibria and the stable phases at 20°. It is the same equilateral triangle of unit height used in the previous papers, in which the respective corners represent 1 mol. of pure anhydrous potassium oleate, 1 mol. of potassium chloride, and 1 kilo. of water; and in which the co-ordinates are the fractions of these three quantities, the sum of which for each point on the diagram is unity. Although not so easily read as the rectangular diagram (Fig. 3), it is much more satisfactory for a complete survey of the field. In Fig. 3 technical units are employed for convenience of comparison with soap-boiling data.

Nearly half of each of Figs. 2 and 3 is occupied by the field of ordinary isotropic solutions. The general form of this extensive field resembles that for sodium palmitate (*loc. cit.*, Figs. 1 and 2), especially if the difference in temperature is taken into account. However, the greater solubility of potassium oleate is reflected in the distinctly larger amounts of salt which can be added without

destroying the homogeneity of the solution. The field of middle soap, though in both cases only approximately delimited, is much more prominent with potassium oleate, whereas the neat soap fields, as far as known, are fairly similar. The field representing crystalline soap is confined to a small part of the uppermost corner of the diagram on account of the low degree of hydration of crystals of potassium oleate. This field likewise requires further study.

In the previous communication (*loc. cit.*, p. 858) the possibility of the existence of a three-phase system, *viz.*, neat soap, nigre and

FIG. 4.



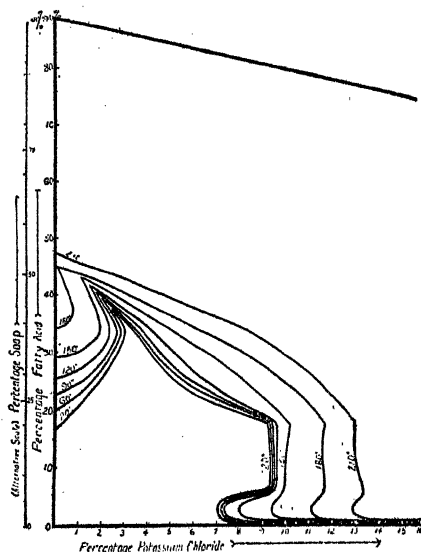
Solubility curves of potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 150°, 180°, and 210° showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures. The point M is the only concentration at which middle soap can exist up to 183°; above this temperature it is isotropic.

lye, is briefly discussed, and it is shown that it is confined to a negligibly narrow region. This is again the finding in the present case, but since a few instances have been met with where apparently these three phases stably co-exist over a very narrow range, corresponding provision has been made in Figs. 2 and 3 of the present paper by indicating the very narrow triangle connecting the compositions of these three phases immediately to the right of the projecting portion of the isotropic field. In Fig. 2 of the previous paper this triangle was represented by a single heavy tie-line, whereas, through inadvertence, in Fig. 1 it was omitted altogether.

For practical purposes, whether this region is a single line or such a very narrow triangle is of no importance.

M. C. Field attempted to test this question for us by preparing five solutions each of which was  $0.5N_w$ -potassium oleate and contained amounts of total potassium chloride ranging from  $1.70N_w$  to  $1.99N_w$ . All five exhibited three layers, the proportion of the middle layer being greatest in the first and progressively less in the others and the amount of upper layer changing accordingly. This would at first sight appear to establish the existence of the suggested

FIG. 5.



*Limits of existence, in technical units, of homogeneous isotropic solutions containing potassium chloride and potassium oleate at 20°, 60°, 90°, 120°, 180°, and 210°, showing the two regions in which solutions of pure soap form isotropic solutions at 210°.*

triangular field and give it a maximum width on the diagram extending from fractional proportion of potassium chloride = 0.53 to 0.57. However, the refractive index of the lye as well as of the middle layer changed progressively with the total composition of the system instead of each phase being identical in composition for all cases and varying only in amount. This is, then, direct proof that complete equilibrium was not attained and that the suggested triangle must be much narrower, having a width of only 1% or so of the total width of the diagram.

Figs. 4 and 5 present the isotherms which bound the field of

isotropic solutions at various temperatures from room temperature up to 210°. These have been much more carefully worked out than in the case of palmitate, and in addition to the actual experimental points indicated in the diagram the position of the isotherms was checked by a series of graphs representing cross sections of the triangular space model for various normalities of soap.

Whereas the maximum temperatures at which middle soap can exist are lowered by the addition of salt, sections 11 and 13 of Table II indicate that in neat soap they are not much affected.

*Summary.*

1. The equilibria between the various forms of a potassium soap are very similar to those for a sodium soap.

2. All the soap phases that exist in the three-component system, including salt, are found in the simpler system, soap and water, where also their separation is spontaneous; that is, they "salt out" in the absence of salt and may even be observed at room temperature.

3. The limits of the field of existence of isotropic liquid solutions of potassium oleate with and without potassium chloride have been accurately determined for temperatures up to 210°. This single phase includes wholly crystalloidal solutions and ranges at sufficiently high temperatures from pure water up to pure anhydrous liquid potassium oleate, the two being miscible in all proportions above 300°.

4. Improvements in the methods of optical investigation have enabled progress to be made with the delimitation of the two important anisotropic liquids, neat soap and middle soap. Both neat soap and middle soap are typical conic anisotropic liquids.

Our warm thanks are due to Messrs. Chris. Thomas and Bros., Ltd., who supported this work by awarding to one of us (W. J. E.) a Colston Research Fellowship.

THE UNIVERSITY, BRISTOL.

[Received, November 12th, 1925.]

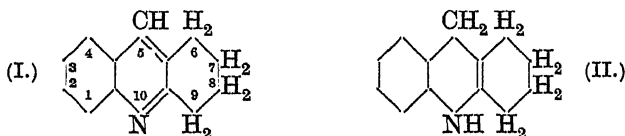
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LVI.—*Tetrahydroacridine, Octahydroacridine, and their Derivatives. Part II. Resolution of the Octahydroacridines (A) and (B).*

By WILLIAM HENRY PERKIN, jun., and WILLIAM GREENWELL SEDGWICK.

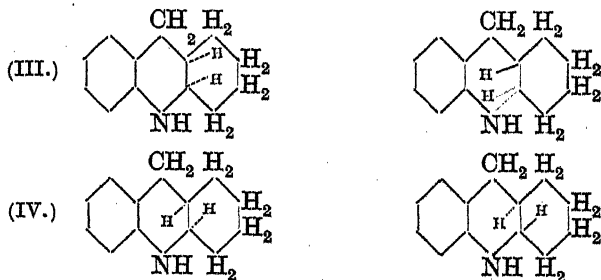
In Part I of this investigation (Perkin and Sedgwick, J., 1924, 125, 2437) it was shown that the reduction of tetrahydroacridine (I) with tin and hydrochloric acid leads at once to the formation of

two octahydroacridines (A, m. p.  $82^\circ$ , and B, m. p.  $72^\circ$ ), four atoms of hydrogen being absorbed. It is remarkable that, in spite of careful search, no intermediate product of reduction could be detected, because it was to be expected that the carbon-nitrogen conjugated system  $\cdot\text{C}:\text{C}:\text{C}:\text{N}\cdot$  would, in the first place, absorb two atoms of hydrogen to yield a hexahydroacridine (II) containing the grouping,  $\geq\text{C}:\text{C}:\text{C}:\text{N}\cdot$ .



Experiment showed that, if less reducing agent is employed than is necessary to convert the whole of the tetrahydroacridine into octahydroacridine, the product is a mixture of octahydroacridine and unchanged tetrahydroacridine. If, as may be assumed to be the case, hexahydroacridine (II) is the intermediate stage, it is probable that this substance is more readily reduced than tetrahydroacridine and is therefore at once converted into octahydroacridine, the corresponding amount of tetrahydroacridine remaining unchanged. It was pointed out in the previous communication (p. 2440) that remarkable as the observation seemed at first, the formation of two octahydroacridines by the addition of four atoms of hydrogen to tetrahydroacridine (I) is strictly in accordance with structural theory.

If the model (compare Sachse, *Ber.*, 1890, **23**, 1363; Mohr, *J. pr. Chem.*, 1918, **98**, 315) be set up and examined, it is at once evident that the pairs (III) and (IV) should result from the addition



of four hydrogen atoms to tetrahydroacridine and that both pairs should be resolvable into their *d*- and *l*-constituents. In order to prove that the configurations (III) and (IV) actually represent the two octahydroacridines (A) and (B), it was clearly necessary to demonstrate that both these substances can be resolved into active constituents. In our first experiments, resolution was attempted

with the aid of bromocamphorsulphonic acid, but without immediate success. It was then discovered that the salts of (A) and (B) with the *d*- and *l*-camphorsulphonic acids are sufficiently well characterised to allow of satisfactory fractional crystallisation, and in this way resolution was achieved in both cases. When the pure salts were decomposed by alkali, they at once yielded the *d*- and *l*-modifications of the octahydroacridines (A) and (B) in a pure state.

The stages in these resolutions will be clearly understood from the following tables :

(I) Resolution of *dl*-Octahydroacridine (A, m. p. 82°).

<i>d</i> -Camphorsulphonic acid	<i>l</i> -Camphorsulphonic acid
↓	↓
1-Octahydroacridine (A) <i>d</i> -camphorsulphonate (m. p. 183°)	<i>d</i> -Octahydroacridine (A) <i>l</i> -camphorsulphonate (m. p. 182°)
NaOH ↓	NaOH ↓
1-Octahydroacridine (A), m. p. 85°, $[\alpha]_D -32^\circ$ .	<i>d</i> -Octahydroacridine (A), m. p. 84.5°, $[\alpha]_D +34^\circ$ .
Mean rotation $[\alpha]_D \pm 33^\circ$ .	

(II) Resolution of *dl*-Octahydroacridine (B, m. p. 72°).

<i>d</i> -Camphorsulphonic acid	<i>l</i> -Camphorsulphonic acid
↓	↓
1-Octahydroacridine (B) <i>d</i> -camphorsulphonate (m. p. 172°)	<i>d</i> -Octahydroacridine (B) <i>l</i> -camphorsulphonate (m. p. 172°)
NaOH ↓	NaOH ↓
1-Octahydroacridine (B), m. p. 73°, $[\alpha]_D -24^\circ$ .	<i>d</i> -Octahydroacridine (B), m. p. 73°, $[\alpha]_D +22^\circ$ .
Mean rotation $[\alpha]_D \pm 23^\circ$ .	

When the corresponding *d*- and *l*-modifications are mixed, the inactive forms are at once produced, but loss of activity also occurs gradually when the *d*- or *l*-modifications are heated at or above their melting points and the change to the inactive form is complete on distillation under reduced pressure. It is curious, both in the case of (A) and of (B), that the inactive modification melts at a somewhat lower temperature than the active constituents, suggesting that the *dl*-modification may be a mixture and not a true racemic compound. It is interesting also that, on boiling with acetic anhydride, *l*-octahydroacridine (A) is converted into the acetyl derivative of *dl*-octahydroacridine (A) (m. p. 86°) described in the previous communication (p. 2449).

So far, sufficient evidence is not available to enable definite configurations to be assigned to the octahydroacridines (A) and (B),

but it is significant that, when tetrahydroacridone is reduced by sodium amalgam (*loc. cit.*, p. 2449), the product consists entirely of modification (A). The probability in this reduction is that the hydrogen atoms will add themselves on to the double linking in the direction indicated in (III) and we are for this reason inclined to assign the configuration (III) to octahydroacridine (A). In the earlier communication (p. 2450) it is shown that isatin condenses with *cyclohexanone* to yield tetrahydroacridinecarboxylic acid (compare Borsche, *Ber.*, 1908, 41, 2207) and that this acid yields, on reduction with sodium amalgam, a mixture of octahydroacridinecarboxylic acids (A) and (B), which, on distillation, decompose with elimination of carbon dioxide and formation of the octahydroacridines (A) and (B). These acids are doubtless also *dl*-modifications corresponding to (III) and (IV) and experiments on their resolution are in progress.

During the course of these resolution experiments, we thought it desirable to be able to confirm the results obtained with the octahydroacridines (A) and (B) by the investigation of another case of the same kind. We therefore condensed 1-methyl*cyclohexan-3-one* with (i) *o*-aminobenzaldehyde and (ii) isatin. In (i) we obtained a substance melting at 71° which may be either 6- or 8-methyltetrahydroacridine and in (ii) a 6(or 8)-methyltetrahydroacridinecarboxylic acid (m. p. 296°) which, on heating, yielded the same parent substance melting at 71°. When this substance is reduced with tin and hydrochloric acid, it is converted into a mixture of 6(or 8)-methyl-octahydroacridines (A, m. p. 92°) and (B, m. p. 80°), and again (compare above) only the modification (A) is produced when 6(or 8)-methyltetrahydroacridone (*loc. cit.*, p. 2442) is reduced with sodium amalgam. Of these modifications, the substance (A) has been resolved with the aid of the *d*- and *l*-camphorsulphonic acids and the active modifications have  $[\alpha]_D + 20^\circ$  and  $- 28^\circ$ , respectively, or a mean rotation of  $[\alpha] \pm 24^\circ$ .

#### EXPERIMENTAL.

The *l*-camphorsulphonic acid used in this research was prepared by sulphonating *l*-camphor with a mixture of sulphuric acid and acetic anhydride as described by Reychler (*Bull. Soc. chim.*, 1898, 111, 120). The *d*-acid was supplied by the British Drug Houses. Both gave physical constants in good agreement with those quoted in the literature, melting, in the anhydrous form, at 193° and showing, in solution as ammonium salts,  $[\alpha]_D \pm 19.9^\circ$ . The octahydroacridine (A) (m. p. 82°) used in the following experiments was obtained partly by the reduction of tetrahydroacridone with sodium amalgam, and both the (A) and (B) modifications were prepared

in quantity by the reduction of tetrahydroacridine and separated by the sulphuric acid method (compare Perkin and Sedgwick, *loc. cit.*, p. 2448).

*Resolution of dl-Octahydroacridine (A)* (m. p. 82°).—This *dl*-base (20 g.), dissolved in the minimum quantity of hot alcohol, was added to a concentrated solution of the equivalent quantity of *d*-camphorsulphonic acid (24.9 g.), and the mixture left over-night. The mother-liquor was then decanted from the crystalline mass of crude 1-octahydroacridine (A) *d*-camphorsulphonate, the crystals (24 g.) were quickly washed with a little alcohol, dissolved in the minimum quantity of boiling alcohol, and allowed to recrystallise. This operation was repeated four times, the final product, 1-octahydroacridine (A) *d*-camphorsulphonate (8 g.), separating in large, colourless prisms, m. p. 182° (Found: C, 65.4; H, 7.7.  $C_{13}H_{17}N, C_{10}H_{15}O \cdot SO_3H$  requires C, 65.9; H, 7.9%; 0.6084 required 14.55 c.c. of *N*/10-NaOH for neutralisation, whereas the theoretical amount is 14.5 c.c.).

In order to separate the free base, the salt was dissolved in alcohol, and the solution carefully neutralised with *N*/10-sodium hydroxide, phenolphthalein being used as indicator; the precipitation was then completed by the addition of water, and the base extracted three times with ether. The ethereal extract was dried over sodium sulphate and concentrated; 1-octahydroacridine (A) then separated slowly in well-defined plates, m. p. 85° (Found: C, 83.2; H, 9.1.  $C_{13}H_{17}N$  requires C, 83.4; H, 9.1%). 0.5 G. in 20 c.c. of alcohol ( $c = 2.5$ ) gave, in a 1-dm. tube,  $\alpha - 0.80^\circ$ , whence  $[\alpha]_D = -32^\circ$ .

*d*-Octahydroacridine (A) was isolated in the same manner by means of *l*-camphorsulphonic acid and melted at 84.5° (Found: C, 83.0; H, 9.0%).  $[\alpha]_D$  in alcohol,  $+34^\circ$  ( $c = 2.5$ ) and in acetone,  $+29^\circ$  ( $c = 2.0$ ). Both active modifications undergo racemisation on distillation and when equal quantities were mixed and the mixture was crystallised from ether, the *dl*-base (A) obtained melted at 82.5°. The melting point of a mixture of approximately equal quantities was 83°. The mother-liquor from the first crystallisation of 1-octahydroacridine (A) *d*-camphorsulphonate deposited, on further concentration, several crops of crystals of varying rotation. The last of these, on repeated recrystallisation, yielded ultimately a crop which was nearly pure *d*-octahydroacridine (A) *d*-camphorsulphonate (m. p. 180°), since the base, set free on neutralisation, had, in alcohol,  $[\alpha]_D + 25^\circ$ .

*Resolution of dl-Octahydroacridine (B)* (m. p. 72°).—This *dl*-base (10 g.) was slowly dissolved in a warm concentrated aqueous solution of *d*-camphorsulphonic acid (15 g.), the excess of acid over



that theoretically required to neutralise the base (12.4 g.) being necessary to effect complete solution. After 12 hours, the crystalline mass was collected, washed with alcohol, and dried between blotting paper, the filtrate (O) being preserved for subsequent treatment.

The crude *l*-octahydroacridine (B) *d*-camphorsulphonate crystallised from water with one molecule of the solvent, which was removed by drying in a desiccator over sulphuric acid or by heating in an air-oven.

The salt was then subjected to two crystallisations from alcohol; the ultimate yield of pure anhydrous *l*-octahydroacridine (B) *d*-camphorsulphonate was 4 g. and the salt melted at 172° with previous softening. 0.4693 G. of the salt required 11.1 c.c. of *N*/10-sodium hydroxide for neutralisation, whereas the theoretical amount is 11.2 c.c.

*l*-Octahydroacridine (B) was obtained from this salt by neutralisation with sodium hydroxide and separated from petroleum (b. p. 40—60°) in colourless plates, m. p. 73° (Found: C, 83.1; H, 9.5.  $C_{13}H_{17}N$  requires C, 83.4; H, 9.1%).  $[\alpha]_D$  in alcohol ( $c = 2.5$ ),  $-24^\circ$ ;  $[\alpha]_D$  in acetone ( $c = 1.0$ ),  $-19^\circ$ .

The filtrate (O), after removal of the crystals which had separated on further standing, was neutralised with sodium hydroxide, and the precipitated base extracted with ether. The ethereal extract was evaporated in a vacuum desiccator, and the crystalline residue (4 g.) showed a small dextrorotation in alcoholic solution.

This material was combined with *l*-camphorsulphonic acid under the conditions already described, the salt purified by repeated crystallisation, and the *d*-octahydroacridine (B) precipitated by neutralisation with sodium hydroxide. The base melted at 73° and had  $[\alpha]_D$  in alcohol ( $c = 2$ )  $+22^\circ$ .

The salts of octahydroacridine (B) with the camphorsulphonic acids are more soluble than those of the isomeride (A), particularly in anhydrous alcohol. This property may be utilised as a method for the separation of the two isomerides, in which case the mixture resulting from the reduction of tetrahydroacridine with tin and hydrochloric acid (*loc. cit.*, p. 2448) is dissolved in a warm concentrated alcoholic solution of the equivalent quantity of *d*-camphorsulphonic acid and allowed to crystallise. The first crop of crystals consists of almost pure octahydroacridine (A) *d*-camphorsulphonate and can be used directly for the resolution of the base.

6(or 8)-Methyltetrahydroacridine.—In preparing this substance, a mixture of *o*-aminobenzaldehyde (3 g.) with 1-methylcyclohexan-3-one (5 g.) was heated in an oil-bath at 100° for about an hour and then at 130° for 1½ hours. On distilling the product under

reduced pressure (15 mm.), water and unchanged methylcyclohexanone passed over below  $120^{\circ}$  and then *methyltetrahydroacridine* (3 g.) distilled at about  $150^{\circ}$  as a pale yellow oil which quickly solidified. The base crystallised from petroleum in colourless plates, m. p.  $70-71^{\circ}$  (Found: C, 85.0; H, 7.5.  $C_{14}H_{15}N$  requires C, 85.3; H, 7.6%). The *picrate*, prepared by mixing solutions of the base and picric acid in hot alcohol, crystallised on cooling in yellow prisms, m. p.  $182^{\circ}$  (darkening).

6(or 8)-*Methyltetrahydroacridinecarboxylic Acid*.—A solution of isatin (10 g.) in potassium hydroxide (42 c.c. of 30%) was mixed with alcohol (80 c.c.) and 1-methylcyclohexanone (20 g.) and refluxed for 12 hours. The alcohol was evaporated in an open basin, the viscid residue mixed with water, the semi-crystalline scum removed by filtration, and the *methyltetrahydroacridinecarboxylic acid* precipitated as a fine, yellow, crystalline powder by the addition of 50% acetic acid.

The dried product is pure enough for most purposes and is very sparingly soluble in the usual solvents. It separates from much alcohol in minute, yellow needles, m. p.  $296^{\circ}$  (decomp.) (Found: C, 74.8; H, 6.6.  $C_{15}H_{15}O_2N$  requires C, 74.7; H, 6.2%). The acid (10 g.) was heated in a distilling flask at its melting point until evolution of carbon dioxide had ceased and the dark liquid was then distilled under 15 mm. pressure; 6(or 8)-*methyltetrahydroacridine* passed over as a pale yellow oil which immediately crystallised. The recrystallised material melted at  $70-72^{\circ}$  and gave no depression of melting point when mixed with a specimen prepared by the *o*-aminobenzaldehyde process just described.

*The 6(or 8)-Methyloctahydroacridines*.—Methyltetrahydroacridine was reduced with tin and hydrochloric acid under the conditions described in the case of tetrahydroacridine (*loc. cit.*, p. 2448), and the resulting two methyloctahydroacridines (A) and (B) were separated in a manner similar to that employed in the separation of the octahydroacridines (A) and (B) (*loc. cit.*). *Methyloctahydroacridine* (A) was also obtained by the reduction of methyltetrahydroacridone and separated from ether or petroleum in colourless prisms, m. p.  $92^{\circ}$ . It was resolved with the aid of *d*- and *l*-camphorsulphonic acids exactly as described in the case of the octahydroacridines (A) and (B). The *d*- and *l*-isomerides melt at  $92^{\circ}$  (Found for the *d*-isomeride: C, 83.4; H, 9.4.  $C_{14}H_{19}N$  requires C, 83.6; H, 9.5%). 0.09 G. of the *d*-modification, dissolved in 15 c.c. of alcohol ( $c = 0.6$ ), gave in a 1-dcm. tube,  $\alpha = +0.12^{\circ}$ , whence  $[\alpha]_D + 20^{\circ}$ . 0.1 G. of the *l*-modification, dissolved in 20 c.c. of alcohol ( $c = 0.5$ ), gave in a 2-dcm. tube,  $\alpha - 0.28^{\circ}$ , whence  $[\alpha]_D - 28^{\circ}$ ; the mean rotation is therefore  $[\alpha]_D \pm 24^{\circ}$ .

The sulphate of *dl*-methyloctahydroacridine (B) is more readily soluble than the sulphate of the modification (A), and the base melts at  $80^\circ$ ; no attempt was made to resolve it into its active modifications.

One of us (W. G. S.) desires to express his thanks to the Salters' Institute of Industrial Chemistry for a Fellowship which has enabled him to engage in this investigation.

THE DYSON PERRINS LABORATORY, OXFORD.

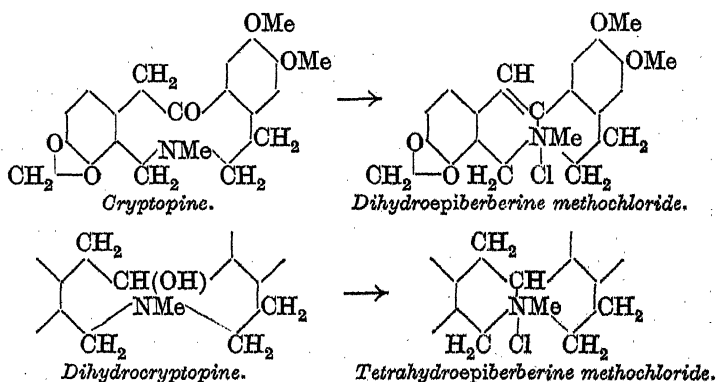
UNIVERSITY COLLEGE, LONDON.

[Received, December 28th, 1925.]

## LVII.—The Conversion of Berberine into $\beta$ -Homochelidonine (*α*-alloCryptopine).

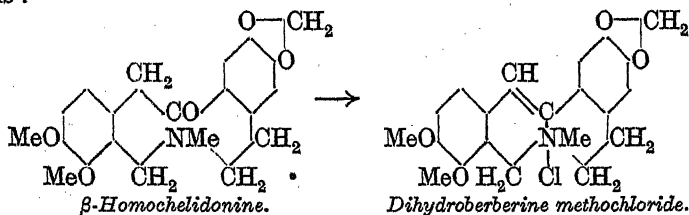
By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

DURING the course of the investigation of cryptopine and protopine (Perkin, J., 1916, 109, 815; 1918, 113, 493, 722; 1919, 115, 713) it was shown that these alkaloids contain a ten-membered ring, and that cryptopine and dihydrocryptopine are converted into quaternary chlorides, containing the berberine skeleton, when they are treated with phosphorus oxychloride :



Subsequently Gadamer (*Arch. Pharm.*, 1919, 257, 298; 1920, 258, 148) found that  $\beta$ -homochelidonine, one of the alkaloids occurring in *Sanguinaria canadensis* and *Chelidonium majus*, is converted into dihydroberberine methochloride, and dihydro- $\beta$ -homochelidonine into tetrahydroberberine methochloride under similar conditions. Gadamer therefore concluded that  $\beta$ -homochelidonine must, like cryptopine, contain a ten-membered ring and that the

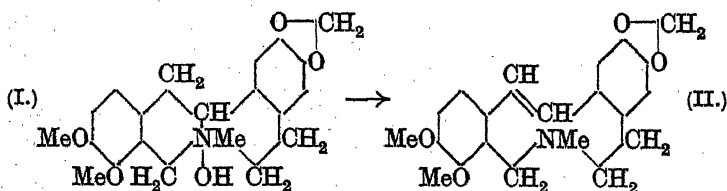
change into dihydroberberine methochloride is to be represented thus:



It is in view of this close relationship that Gadamer (*loc. cit.*) suggested the name  $\alpha$ -allocryptopine for  $\beta$ -homochelidonine.

The synthesis of berberine recently achieved by Perkin, Ray, and Robinson (J., 1925, 127, 740; compare Späth, *Ber.*, 1925, 58, 2268) will, it is hoped, serve as a basis for the synthesis of other alkaloids of similar constitution and it now became important to devise a method which would enable synthetical alkaloids of the berberine type to be converted into alkaloids like cryptopine, protopine, and  $\beta$ -homochelidonine with which they are clearly closely allied. The present investigation is concerned with such a method, namely, with the conversion of berberine into  $\beta$ -homochelidonine. The development of the process to the synthesis of cryptopine and the allied alkaloids will, it is hoped, form the subject of future communications.

It has long been known (Voss and Gadamer, *Arch. Pharm.*, 1910, 248, 43; Freund, *Annalen*, 1913, 397, 1; Pyman, J., 1913, 103, 817; McDavid, Perkin, and Robinson, J., 1912, 101, 1220; Perkin, J., 1916, 109, 952) that tetrahydroberberine methohydroxide (I) loses water when its aqueous solution is evaporated in a vacuum and yields as chief product anhydrotetrahydromethylberberine (anhydromethylcanadine) (II), a remarkable change which results in the formation of a substance containing a ten-membered ring and in which the various groups occupy the same relative positions as in  $\beta$ -homochelidonine.



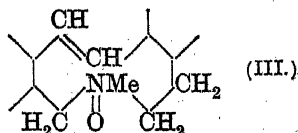
It is clearly only necessary to convert the group  $\cdot\text{CH}:\text{CH}\cdot$  in the latter formula into  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  in order to achieve the synthesis of  $\beta$ -homochelidonine.

The realisation of this comparatively simple change proved to be a very difficult problem, mainly because the usual methods are not applicable to anhydrotetrahydromethylberberine. This substance exhibits a remarkable tendency, when treated with many of the usual reagents, and indeed merely on boiling with alcohol or chloroform, to revert to tetrahydroberberine methohydroxide or its salts with consequent loss of the ten-membered ring (compare Pyman, *loc. cit.*, p. 834). We observed the same change when an ice-cold solution of the base in chloroform was treated with bromine, since the crystalline perbromide which separated yielded tetrahydroberberine methobromide on decomposition with sulphurous acid. A series of experiments on the action of oxidising agents on anhydrotetrahydromethylberberine did not lead to the desired result, although interesting oxidation products were obtained, when this base was treated with silver hydroxide or hydrogen peroxide, which will be discussed in a future communication.

Some years since (*Ber.*, 1909, 42, 4811; 1910, 43, 959), Prileschajew carried out an important piece of work in the course of which he showed that ethylene derivatives,  $\cdot\text{CH}=\text{CH}\cdot$ , yield

ethylene oxides,  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}-\text{CH} \end{array}$ , on treatment with perbenzoic acid, and it seemed probable that, if this change could be brought about in the case of anhydrotetrahydromethylberberine, the resulting ethylene oxide grouping might be made to isomerise to  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  and thus lead to the formation of  $\beta$ -homochelidonine (compare Weitz and Scheffer, *Ber.*, 1921, 54, 2344).

When an ice-cold solution of the base (II) in chloroform is added to an ice-cold solution of perbenzoic acid, the ethylene oxide derivative does not appear to be produced. Oxidation takes place rapidly, however, and a base,  $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$ , isomeric but not identical with  $\beta$ -homochelidonine, is obtained in good yield. This curious substance crystallises from water, decomposes at  $135^\circ$ , and yields a hydrochloride,  $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}\cdot\text{HCl}$ , which is sparingly soluble in water. These and other properties seem to indicate that it is an amine oxide containing the group



In connexion with the formation and properties of this substance, it is interesting to note that Meisenheimer (*Ber.*, 1919, 52, 1667) has observed that perbenzoic acid converts methylallylaniline into the amine oxide,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{NMePh}\cdot\text{O}$ , without affecting the

ethylenic linking of the allyl group. He shows that this amine oxide undergoes a curious isomeric change to phenylmethylallyl-hydroxylamine,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{-O}\cdot\text{NMePh}$ , when heated with alkalis, and Bamberger and Leyden (*Ber.*, 1901, 34, 12) state that dimethyl-aniline oxide is converted into a mixture of *o*- and *p*-dimethyl-aminophenol by contact with sulphuric acid.

These curious isomeric changes encouraged us to examine in detail the action of various reagents on anhydrotetrahydromethylberberine oxide (III) and it was ultimately observed that in the presence of glacial acetic acid and hydrochloric acid, this amine oxide isomerises to a basic substance which crystallises from ethyl acetate in colourless prisms, m. p. 160—161°, and is identical with  $\beta$ -homochelidonine. The synthetic alkaloid gave no depression in m. p. when mixed with a specimen of  $\beta$ -homochelidonine, for which we are indebted to Professor Gadamer; the hydrochloride was readily soluble in water and crystallised from alcohol-ether in colourless needles which were identical in appearance and behaviour with the hydrochloride of the naturally occurring alkaloid. The garnet-red aurichloride, m. p. 190—192° (decomp.), had all the properties of the double salt prepared from the natural product, whilst the colour reactions of the synthetic and the natural alkaloid with concentrated sulphuric acid, Fröhde's, and Erdmann's reagents were indistinguishable. We propose to investigate the mechanism of the above synthesis, more particularly in regard to the action of other reagents on the amine oxide, and details of this work as well as of the extension of the method to the synthesis of cryptopine, protopine, and allied alkaloids are reserved for a later communication.

#### EXPERIMENTAL.

Anhydrotetrahydromethylberberine was prepared as recommended by Pyman (*loc. cit.*, p. 833), but we found it advisable to use as little excess of silver hydroxide as possible in the preparation of tetrahydroberberine methohydroxide. Tetrahydroberberine methiodide, dissolved in boiling water, is agitated for  $\frac{1}{2}$  hour with the calculated amount of silver hydroxide, and the solution is filtered hot and tested for unchanged methiodide with silver nitrate. If iodide is still present, a further small quantity of silver hydroxide is added and the process repeated if necessary. The whole is then filtered and the solution evaporated exactly as described by Pyman. The perbenzoic acid used in these experiments was prepared by the method of Baeyer and Villiger (*Ber.*, 1900, 33, 1575). It was extracted with ether and the content of the ethereal solution

estimated, immediately before use, by titration with potassium iodide and *N*/10-sodium thiosulphate.

*Anhydrotetrahydromethylberberine Oxide*.—Anhydrotetrahydromethylberberine (2 g.), dissolved in dry chloroform, was gradually added to a solution of perbenzoic acid (estimated as 1.8 g.) in ether (100 c.c.), maintained below 5° by immersion in ice. An oil gradually separated which sometimes crystallised on standing. After remaining over-night, the mixture was shaken with 10% sodium hydroxide; the amine oxide then solidified as a white solid (1.5 g.) and was collected after several hours. A second crop may be obtained from the filtrate by the careful addition of strong sodium hydroxide.

*Anhydrotetrahydromethylberberine oxide* crystallises from water in colourless, slender prisms, m. p. 135° (decomp.) (Found: C, 68.1; H, 6.5.  $C_{21}H_{23}O_5N$  requires C, 68.3; H, 6.2%). It is soluble in chloroform or acetic acid, moderately easily soluble in ethyl acetate, and almost insoluble in ether or petroleum. It dissolves in hot water, but is less soluble in sodium hydroxide solution. On cooling the solution of the base in hot dilute hydrochloric acid, the *hydrochloride* separates in colourless nodules, m. p. 203° (decomp.) with previous darkening. It is more soluble in water than in dilute hydrochloric acid (Found: C, 62.2; H, 6.0.  $C_{21}H_{23}O_5N \cdot HCl$  requires C, 62.1; H, 5.9%).

*$\beta$ -Homochelidonine*.—The amine oxide (1.5 g.), dissolved in glacial acetic acid (10 c.c.) and concentrated hydrochloric acid (5 c.c.), was heated in rapidly boiling water for an hour, the pale yellow solution diluted with water, made alkaline with potassium hydroxide,\* and the cream-coloured solid collected. This was dissolved in methyl alcohol (20 c.c.), mixed with ether (200 c.c.), the ethereal solution washed with water until free from methyl alcohol, rapidly dried over potassium carbonate, and concentrated to a small bulk. On standing,  $\beta$ -homochelidonine separated; it crystallised from ethyl acetate in brilliant, colourless, monoclinic prisms, m. p. 160–161° (Found: C, 68.3; H, 6.5. Calc. for  $C_{21}H_{23}O_5N$ : C, 68.3; H, 6.2%). The crystals were exactly like those of a specimen of  $\beta$ -homochelidonine which Professor Gadamer very kindly sent us and there was no change in melting point when the two specimens were mixed.

Synthetic  $\beta$ -homochelidonine dissolves in concentrated sulphuric

\* The base is not completely precipitated from its salts by the addition of ammonia, and this property of  $\beta$ -homochelidonine is made use of in the isolation of the alkaloid from the plant (Schmidt and Selle, *Arch. Pharm.*, 1890, 228, 441).

acid to a yellow solution which rapidly becomes violet and slowly changes to bright red. With Fröhde's reagent, a yellow solution is obtained which soon becomes violet and then passes through brilliant blue to bluish-green. The base dissolves in Erdmann's reagent to a yellow solution which rapidly becomes violet and then dirty violet. These colour reactions are indistinguishable from those exhibited by the specimen of naturally occurring  $\beta$ -homochelidonine under similar conditions. The hydrochloride was obtained by dissolving the base in dilute hydrochloric acid and evaporating to dryness. The residue dissolved readily in alcohol and, on addition of ether, the hydrochloride slowly separated in slender, colourless, silky needles which turn yellow and shrink at about  $170^{\circ}$  and decompose at about  $190^{\circ}$ . The hydrochloride of the natural alkaloid possessed identical properties. The aurichloride separated on addition of gold chloride to the solution of the base in dilute hydrochloric acid, and crystallised from alcohol in warts of garnet-red crystals, m. p.  $190-192^{\circ}$  (decomp.). No alteration in m. p. was observed when this sample was mixed with the garnet-red aurichloride prepared in the same way from natural  $\beta$ -homochelidonine.

One of us (R. D. H.) desires to thank the Commissioners of the 1851 Exhibition for a studentship, and the Government Grant Committee of the Royal Society and the Research Fund Committee of the Chemical Society for grants towards the expense of this investigation.

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OXFORD.

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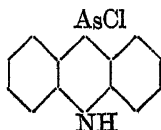
LVIII.—10-Chloro-5:10-dihydrophenarsazine and its Derivatives. Part I. The Synthesis, Preparation, and Some Properties of 10-Chloro-5:10-dihydrophenarsazine.

By HAROLD BURTON and CHARLES STANLEY GIBSON.

THE reaction between arsenious halides and secondary aromatic amines was the subject of a patent of F. Bayer & Co. (D.R.-P. 281049, Friedländer, "Fortschritte," 1914, XII, 843), and Wieland and Rheinheimer (*Annalen*, 1921, 423, 1) made a comprehensive study of the derivatives of the compound obtained by condensing arsenious chloride and diphenylamine. To this compound, Wie-

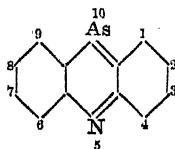


land and Rheinheimer gave the name "phenarsazine chloride" and ascribed to it the constitution



which is the same as that ascribed to it by the patentees.\*

\* Wieland and Rheinheimer (*loc. cit.*) prepared the compound phenarsazine, which undoubtedly has the structure



The product of the reaction between diphenylamine and arsenious chloride is derived from phenarsazine by the addition of hydrogen chloride. This compound has hitherto been variously known as "diphenylamine arsenious chloride" (Contardi, *Giorn. Chim. Ind. Appl.*, 1920, i, 11; ii, 100), "phenarsazine chloride" (Wieland and Rheinheimer, *loc. cit.*), and "6-chlorophenarsazine" (Lee Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, 43, 2218; Lee Lewis, Lowry, and Bergeim, *ibid.*, p. 891). In systematically describing this class of compounds, the name phenarsazine is retained for the parent substance and the atoms are numbered as indicated. The product of the reaction between diphenylamine and arsenious chloride and its simple derivatives are regarded as substitution products of 5:10-dihydrophenarsazine, at present unknown. "Phenarsazinic acid," which is already in use for the oxidation product of these derivatives, still applies.

Although the patent referred to was taken out in 1913 and issued in the German Empire in December, 1914, the specification was not available in this country until September, 1920. Our knowledge of this type of heterocyclic compound up to 1918 was limited to that contained in a brief abstract of the patent, which referred only to the general reaction between arsenious chloride and diarylamines without mentioning any specific compound (*J. Soc. Chem. Ind.*, 1915, 34, 636). It ought to be pointed out that Dr. W. C. Ball independently prepared the compound early in 1918 (unpublished report of the Anti-gas Department) by the action of arsenious chloride on diphenylamine and examined a number of its simpler derivatives. Professor G. T. Morgan in 1918 (unpublished report) also studied the reaction and prepared certain analogues of 10-chloro-5:10-dihydrophenarsazine. In preparing his "diphenylamine arsenious chloride," Contardi (*loc. cit.*) heated diphenylamine hydrochloride and arsenious oxide together in the proportions for the following reaction to take place:

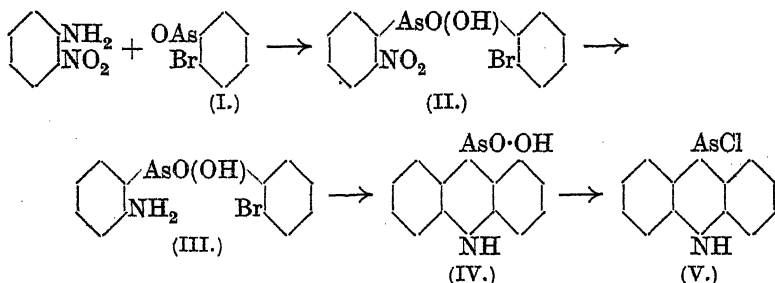


The reaction as described by Contardi does take place, but we have not been able to obtain the high yield recorded, probably because the product of the reaction is decomposed rapidly by water at the temperature employed.

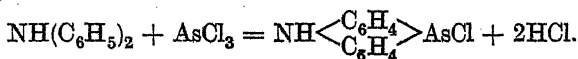
The compound so easily obtained in almost quantitative yield by heating

The work now described was in progress before the paper by Wieland and Rheinheimer (*loc. cit.*) was available, and it seems desirable to describe our results, which supplement those of these two workers.

The constitution ascribed to 10-chloro-5 : 10-dihydrophenarsazine has been proved to be correct by the following synthesis, which may be represented diagrammatically :



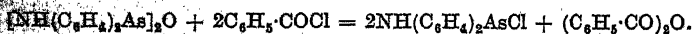
The first stage consisted in diazotising *o*-nitroaniline and coupling the diazo-compound with *o*-bromophenylarsenious oxide (I). The resulting compound, 2-bromo-6'-nitrodiphenylarsinic acid, is reduced to the corresponding amino-compound (III) by means of ferrous hydroxide. By heating in amyl alcohol with potassium carbonate and a small quantity of copper powder, the amino-compound is readily converted into phenarsazinic acid (IV), and this, when reduced in hydrochloric acid-alcohol solution by sulphur dioxide, is readily converted into 10-chloro-5:10-dihydrophenarsazine identical with the substance prepared by the action of arsenious chloride on diphenylamine according to the equation



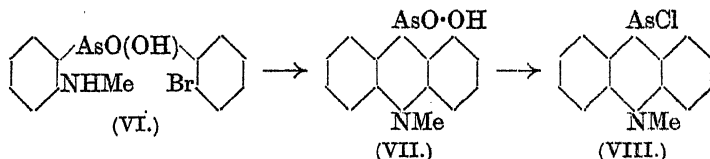
The preparation by Burton and Gibson (J., 1924, **125**, 2277) of the *N*-acetyl, *N*-propionyl, and *N*-benzoyl derivatives is confirmatory evidence of the presence of the :NH group in 10-chloro-5 : 10-dihydrophenarsazine.\* Wieland and Rheinheimer (*loc. cit.*) also have described the preparation of the *N*-methyl derivative from

together arsenious chloride and diphenylamine under the conditions described by previous workers is systematically described as 10-chloro-5:10-dihydro-phenarsazine.

\* Whilst 10:10'-oxy-5:10-dihydrophenarsazine reacts with acetyl chloride to give 10-chloro-5-acetyl-5:10-dihydrophenarsazine, benzoyl chloride and the oxy-compound react quantitatively as follows:



arsenious chloride and *N*-methyldiphenylamine. In connexion with our work on the phenarsazinic acids of this group of compounds, it was important to prepare the corresponding acid (Burton and Gibson, *loc. cit.*) with a view to investigate its trypanocidal properties. The only substance we have obtained by condensing arsenious chloride with *N*-methyldiphenylamine and working up the product under the conditions described by Wieland and Rheinheimer is 10-chloro-5 : 10-dihydrophenarsazine and not 10-chloro-5-methyl-5 : 10-dihydrophenarsazine (the *N*-methyl derivative). The melting point of the material we isolated from this reaction (about 10% of the theoretical quantity) was unaffected on admixture with an authentic specimen of 10-chloro-5 : 10-dihydrophenarsazine. Whilst the melting point, quoted by Wieland and Rheinheimer, of the supposed *N*-methyl derivative is 203° (some 8—10° higher than that of 10-chloro-5 : 10-dihydrophenarsazine), its further characterisation is somewhat inconclusive.\* Like Wieland and Rheinheimer, we have failed to obtain the *N*-methyl derivative by attempting to methylate 10-chloro-5 : 10-dihydrophenarsazine and we therefore attempted to synthesise the compound according to the following scheme based on the method for obtaining the parent substance :



Whether the compound (VII) is actually formed we are unable to say, but when the product obtained by heating 2-bromo-6'-methylaminodiphenylarsinic acid (VI) in amyl alcohol with potassium carbonate and copper powder is reduced in hydrochloric acid-alcohol solution with sulphur dioxide 10-chloro-5:10-dihydrophenarsazine, *o*-bromophenylarsenious chloride and methylaniline are obtained (see p. 459). While the *N*-acyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine are prepared quite readily, the fact that we have been unable to prepare the *N*-methyl derivative either directly or by synthesis is not easily explained.

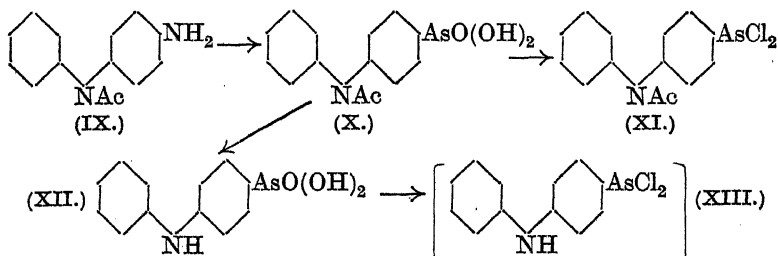
The most convenient way for preparing 10-chloro-5 : 10-dihydrophenarsazine in the laboratory is by heating one molecular proportion of diphenylamine with rather more than one molecular proportion of freshly distilled arsenious chloride in dichlorobenzene. The

\* The micro-analysis quoted by the above authors showed a nitrogen content of 5.0%, the calculated values for  $\text{NH}(\text{C}_6\text{H}_4)_2\text{AsCl}$  and  $\text{NMe}(\text{C}_6\text{H}_4)_2\text{AsCl}$  being 5.05 and 4.95% of nitrogen, respectively.

product crystallises from the solution on cooling and is rapidly purified by extraction with carbon tetrachloride. The fact that the reaction between arsenious chloride and diphenylamine takes place slowly at the ordinary temperature \* (actually a yield of 10% of the theoretical was obtained after 16 months) has enabled us to study the reaction somewhat closely. When the two reacting substances are mixed in the presence of a solvent, a white, crystalline substance having the composition  $\text{HCl} \cdot \text{NH}(\text{C}_6\text{H}_5)_2 \cdot \text{AsCl}_3$ , is slowly deposited. In a sealed apparatus no development of pressure was recorded, but the solution became dark green and crystals of 10-chloro-5:10-dihydrophenarsazine were slowly deposited. The same white crystalline substance was formed immediately on mixing diphenylamine hydrochloride and arsenious chloride, but no further reaction took place. On heating a mixture of arsenious chloride and diphenylamine or its hydrochloride in high-boiling solvents, the additive compound dissolves, a copious evolution of hydrogen chloride takes place, and 10-chloro-5:10-dihydrophenarsazine is rapidly formed. From these results, it appears that at the ordinary temperature diphenylamine and arsenious chloride react to liberate hydrogen chloride which combines with unchanged diphenylamine, forming its hydrochloride which then crystallises as the additive compound with arsenious chloride. The substitution product is soluble and has not been isolated, but it is clear that this soluble compound is intermediate in the formation of the final product. If the mixture is not heated and no escape for the hydrogen chloride is provided, it is obvious that the reaction cannot go to completion. In view of the results of the large number of investigations on the action of arsenious chloride on aniline (summarised by Schmidt, *J. Amer. Chem. Soc.*, 1921, 43, 2449) it is quite probable that the soluble intermediate compound may have the composition  $(\text{C}_6\text{H}_5)_2\text{N} \cdot \text{AsCl}_2$ . The ease of formation of 10-chloro-5:10-dihydrophenarsazine is very striking in view of the fact that usually para-substitution takes place when arsenic is introduced into the nucleus of aromatic amines. This is the case, not only in the formation of arsanilic acid, but also when arsenious chloride reacts with dialkylanilines (Michaelis and Rabinerson, *Annalen*, 1892, 270, 139; Michaelis, *Ber.*, 1908, 41, 1514); with monoalkylanilines and arylglycines (Poulenc Frères and Oechsli, French Patents 450214, 462276, and 473704). The following scheme of reactions was therefore studied with a view to the preparation of *p*-phenylaminophenylarsenious chloride (diphenylamine-*p*-arsenious chloride), which obviously

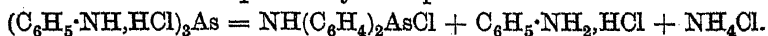
\* The investigation of the reaction between diphenylamine and arsenious chloride at the ordinary temperature was carried out by the late Mr. D. C. Vining and one of us (C. S. G.).

cannot be prepared directly from arsenious chloride and diphenylamine :

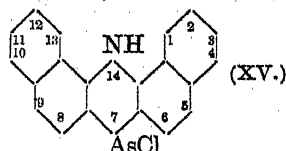
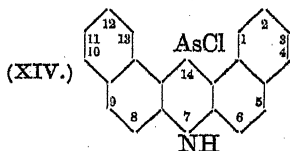


The reduction of the arsenic acid (XII) in the usual manner causes the elimination of the arsenic, and diphenylamine is the main product of the reaction. Consequently it has not been possible to prepare *p*-phenylaminophenylarsenious chloride (XIII), although its *N*-acetyl derivative (XI) is easily obtainable. In view of the ease with which 10-chloro-5:10-dihydrophenarsazine is obtained, this result is not unexpected.

In studying the action of arsenious chloride on aniline, Schmidt (*loc. cit.*) isolated trianilinoarsine hydrochloride,  $(\text{C}_6\text{H}_5\cdot\text{NH}_2\cdot\text{HCl})_3\text{As}$ , which was first described by Schiff (*Compt. rend.*, 1863, 56, 268, 1095). By heating this compound for a long time, either alone or in the presence of an excess of aniline, Schmidt claimed to have obtained 10-chloro-5:10-dihydrophenarsazine, which he identified as the corresponding oxy-compound.\* Schmidt states that the reaction which takes place may be expressed as follows :



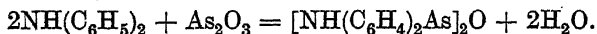
Since we have been able to isolate diphenylamine from the product obtained by heating the trianilinoarsine hydrochloride with an excess of aniline, it is possible that the formation of 10-chloro-5:10-dihydrophenarsazine may be due to the action of arsenious chloride on diphenylamine which is formed under these conditions. This possibility is supported by the fact that when arsenious chloride and  $\beta$ -naphthylamine are heated together in *o*-dichlorobenzene solution 14-chloro-14:7-dihydrodibenzophenarsazine (XIV)



\* Schmidt states that the oxy-compound is crystallised from acetic acid. It has been known for some time (Wieland and Rheinheimer, *loc. cit.*) that under such conditions the oxy-compound is converted into the 10-acetyl-5:10-dihydrophenarsazine.

is readily obtained with elimination of ammonium chloride, and is identical with the product obtained by heating di- $\beta$ -naphthylamine with arsenious chloride under identical conditions (D.R.-P., *loc. cit.*).  $\alpha$ -Naphthylamine and arsenious chloride do not react to give a compound analogous to 10-chloro-5:10-dihydrophenarsazine; the compound 7-chloro-7:14-dihydrodibenzophenarsazine (XV) is, however, readily obtained from di- $\alpha$ -naphthylamine (D.R.-P., *loc. cit.*).

The ease of the *oo'*-substitution in diphenylamine is also well illustrated by the preparation in good yield of 10:10'-oxy-5:10-dihydrophenarsazine from diphenylamine and arsenious oxide according to the equation:



The reaction takes place readily at temperatures above  $130^\circ$  in the presence of phosphorus pentoxide.

Regarding 10-chloro-5:10-dihydrophenarsazine, one of its most striking properties is its power of forming molecular compounds. Molecular compounds with acetic acid, *s*-tetrachloroethane, chlorobenzene, *o*-dichlorobenzene, acetone, carbon tetrachloride, and arsenious chloride have been isolated.

The chlorine atom in 10-chloro-5:10-dihydrophenarsazine can be easily replaced by other atoms or groups. Some of these derivatives have been described by Wieland and Rheinheimer (*loc. cit.*). The most convenient way of preparing the corresponding bromo- and iodo-compounds—we have not succeeded in preparing the latter compound directly from diphenylamine and arsenious iodide—is by adding the corresponding concentrated halogen acid to the solution of the oxy-compound in acetic acid. The bromo- and iodo-compounds are formed almost quantitatively in a state of purity. The iodo-compound resembles the chloro-compound in showing a similar tendency to form molecular compounds with, for example, benzene and acetic acid. Wieland and Rheinheimer noticed the solubility of the oxy-compound in methyl alcohol and isolated the colourless 10-methoxy-5:10-dihydrophenarsazine. The analogous *n*-butoxy- and benzyloxy-compounds described in the present paper are also colourless and being more soluble than the methoxy-derivative are more useful in preparing other derivatives, for example, the sulpho-compound.

#### EXPERIMENTAL.

*o*-Bromophenylarsinic Acid,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{AsO}(\text{OH})_2$ .—*o*-Aminophenylarsinic acid (36 g.) dissolved in hydrobromic acid (126 c.c.; *d* 1.265) and water (63 c.c.) was diazotised at  $0^\circ$  with sodium nitrite (12.6 g.)

in water (25 c.c.). The cold diazo-solution was added gradually, with stirring, to a solution of cuprous bromide at 30–40°. (The cuprous bromide solution was made by boiling 16.5 g. of copper carbonate, 165 c.c. of hydrobromic acid, and copper until the solution was clear.) The solid matter was filtered off, and extracted with hot alcohol. The alcoholic extract was evaporated to dryness, boiled with sodium carbonate solution and filtered. On acidifying with concentrated hydrochloric acid, *o*-bromophenylarsinic acid (27 g.) separated in nearly colourless crystals, m. p. 201° (decomp.). The acid crystallises from aqueous alcohol in colourless prisms, m. p. unchanged (Found: As, 26.4. Calc., As, 26.7%).

*o*-Bromophenylarsenious Oxide (I).—*o*-Bromophenylarsinic acid (14 g.) was dissolved in alcohol (14 c.c.) and concentrated hydrochloric acid (14 c.c.) containing a trace of iodine. Sulphur dioxide was passed into the boiling mixture for 30 minutes; the chloroarsine then separated as a heavy oil. After evaporation of the alcohol, the oil was extracted with benzene. The benzene solution was shaken with ammonia (14 c.c.;  $d$  0.880) and, after the mixture had cooled, the solid matter was filtered off. This was washed with water until free from ammonium chloride and dried. The benzene filtrate on evaporation gave a small quantity of the oxide. The yield was 92.5% of the theoretical. *o*-Bromophenylarsenious oxide is insoluble in most neutral solvents and melts at 234–238° (Found: As, 30.25.  $C_6H_4OBrAs$  requires As, 30.4%).

2-Bromo-6'-nitrodiphenylarsinic Acid (II).—A suspension of *o*-nitroaniline (13.8 g.) in concentrated hydrochloric acid (80 c.c.) and water (250 c.c.) was cooled to 0° and diazotised with a solution of sodium nitrite (7.6 g.) in water. The filtered solution was added with stirring to a solution, at 20°, of *o*-bromophenylarsenious oxide (27.2 g.) in 5*N*-sodium hydroxide solution (174 c.c.) diluted to 500 c.c. with water, and containing 10 c.c. of 10% aqueous copper sulphate solution to which ammonia had been added to form the soluble complex. The mixture was stirred for 2 hours, made faintly acid to litmus, and filtered. On adding concentrated hydrochloric acid to the filtrate, until Congo-paper turned blue, 2-bromo-6'-nitrodiphenylarsinic acid (19.6 g.) was precipitated. It crystallised from dilute alcohol in pale yellow prisms, m. p. 254–255° (decomp.) (Found: Br, 20.9; As, 19.2.  $C_{12}H_9O_4NBrAs$  requires As, 19.4; Br, 20.7%).

2-Bromo-6'-aminodiphenylarsinic Acid (III).—Ferrous hydroxide was precipitated from a hot solution of ferrous sulphate (50 g.) in water (150 c.c.) by adding an excess of 25% sodium hydroxide solution. To the boiling suspension a solution of 2-bromo-6'-nitrodiphenylarsinic acid (11.5 g.) in dilute sodium hydroxide was added

slowly with stirring. The mixture was then boiled for 15 minutes. After filtration from the ferric hydroxide, the colourless solution was acidified with concentrated hydrochloric acid (Congo-paper), and the precipitated amino-acid (9.8 g.) filtered. It crystallised from dilute alcohol in colourless prisms, m. p. 213—214° (decomp.) (Found: As, 20.7; Br, 22.3.  $C_{12}H_{11}O_2NBrAs$  requires As, 21.1; Br, 22.45%).

*2-Bromo-6'-methylaminodiphenylarsinic Acid (VI).*—2-Bromo-6'-aminodiphenylarsinic acid (21.4 g.) was suspended in water (150 c.c.) and mixed with 7.6 g. of methyl sulphate. After thorough mixing, a solution of sodium hydroxide (5 g.) in water (20 c.c.) was added in five portions at intervals of 30 minutes. The mixture was well shaken after each addition. The solution was then acidified with hydrochloric acid, and the crude acid filtered. This was dissolved in the minimum quantity of hot alcohol and allowed to cool; a crop of unchanged material (6.0 g.) was then obtained. The alcoholic solution was evaporated and a fraction (10.8 g.), m. p. 192—193°, obtained. This fraction on recrystallisation from alcohol melted at 193—194° (decomp.) (Found: C, 42.3; H, 3.7; Br, 21.6.  $C_{13}H_{13}O_2NBrAs$  requires C, 42.2; H, 3.5; Br, 21.6%).

*2-Bromo-6'-dimethylaminodiphenylarsinic Acid.*—A mixture of 2-bromo-6'-aminodiphenylarsinic acid (4.3 g.) and methyl sulphate (10 c.c.) was heated on the steam-bath for 3 hours. After decomposition of the resulting solution with sodium carbonate solution, the acid was precipitated by hydrochloric acid. It crystallised from aqueous alcohol in clusters of colourless needles, m. p. 220—221° (decomp.) (Found: C, 43.8; H, 4.2; Br, 21.0.  $C_{14}H_{15}O_2NBrAs$  requires C, 43.75; H, 3.9; Br, 20.8%).

*The Formation of Phenarsazinic Acid (IV) from 2-Bromo-6'-aminodiphenylarsinic Acid. Isolation of 10-Chloro-5:10-dihydrophenarsazine (V).*—A mixture of 2-bromo-6'-aminodiphenylarsinic acid (10.8 g.), dry potassium carbonate (4.4 g.), amyl alcohol (80 c.c.), and a trace of copper powder was boiled under reflux for 12 hours. The amyl alcohol was removed with steam, and the aqueous residue filtered from the copper. The solution was acidified with hydrochloric acid, and the precipitated acid (8.9 g.) filtered off, well washed with water, and dissolved in a mixture of alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) containing a trace of iodine. Sulphur dioxide was passed into the boiling solution for 10 minutes; yellow solid matter then began to separate. After cooling, the crude 10-chloro-5:10-dihydrophenarsazine (8.6 g.) was filtered off and extracted with carbon tetrachloride. This solution, on cooling, deposited yellow needles, melting at 191—192° alone or mixed with an authentic sample of 10-chloro-5:10-dihydrophenarsazine.



*Reduction of 2-Bromo-6'-aminodiphenylarsinic Acid. Isolation of o-Bromophenylarsenious Chloride.*—A hot solution of 2-bromo-6'-aminodiphenylarsinic acid (5 g.) in alcohol (5 c.c.), concentrated hydrochloric acid (5 c.c.), and a trace of iodine was treated with sulphur dioxide for 45 minutes. On cooling, a gummy solid separated which slowly solidified. It was filtered off, and found to be *o*-bromophenylarsenious chloride, m. p. 65–66°, the melting point being unchanged by admixture with an authentic sample. 2-Bromo-6'-methylaminodiphenylarsinic acid and 2-bromo-6'-dimethylaminodiphenylarsinic acid under similar conditions yield methylaniline and dimethylaniline, identified as acetomethylanilide and *p*-nitroso-dimethylaniline, respectively, together with *o*-bromophenylarsenious chloride.

*Attempted Preparation of N-Methylphenarsazinic Acid (VII).*—A mixture of 2-bromo-6'-methylaminodiphenylarsinic acid (11.1 g.), dry potassium carbonate (4.2 g.), amyl alcohol (80 c.c.), and a trace of copper powder was boiled under reflux for 12 hours. After steam distillation of the volatile products the aqueous residue was acidified and the crude acid (6.5 g.) filtered off. This was dissolved in alcoholic hydrochloric acid, and the boiling solution, to which a trace of iodine had been added, was saturated with sulphur dioxide for 20 minutes. A tarry precipitate was obtained which on extraction with carbon tetrachloride gave a crop of yellow needles, m. p. 191°. This substance was 10-chloro-5:10-dihydrophenarsazine, identified by comparison with an authentic sample.

The mother-liquors from the alcoholic hydrochloric acid treatment were evaporated, made alkaline with ammonia, and extracted with ether. This ethereal extract on evaporation gave a small quantity of an oil, smelling of methylaniline. On acetylation a small amount of acetomethylanilide, m. p. 101°, was obtained.

*Action of Arsenious Chloride on Methyl-diphenylamine.*—(a) Attempts to prepare 10-chloro-5-methyl-5:10-dihydrophenarsazine from methyl-diphenylamine and arsenious chloride in the presence of dichlorobenzene resulted in decomposition of the reacting substances and no crystalline matter could be isolated.

(b) Methyl-diphenylamine (36.6 g.) and arsenious chloride (36.2 g.) were heated under reflux at 200° for 2 hours. The coloured residue was cooled, extracted with light petroleum, and the solid residue (46.2 g.) worked up, following as closely as possible the details described by Wieland and Rheinheimer (*loc. cit.*). The only compound isolated (yield 10%) was 10-chloro-5:10-dihydrophenarsazine, m. p. 187–190°, identical in every respect with an authentic specimen.

*10-Chloro-5:10-dihydrophenarsazine.*—A mixture of diphenyl-

amine (17 g.), arsenious chloride (20 g.), and *o*-dichlorobenzene (40 c.c.) was boiled under reflux for 5 hours, hydrogen chloride escaping steadily. On cooling, the dark green solution deposited a mass of crystals which were filtered off, washed with petrol, dried, and crystallised from carbon tetrachloride. 10-Chloro-5:10-dihydrophenarsazine prepared in this way melts at 191—192° and is bright yellow (yield almost theoretical).

*The Reaction between Diphenylamine and Arsenious Chloride at the Ordinary Temperature.*—Arsenious chloride (8.3 g.) was dissolved in dry benzene (10 c.c.) and treated with diphenylamine (7.8 g.). Solution resulted, and after 1 hour crystallisation commenced. After 24 hours the crystalline matter was filtered off rapidly in the absence of air, washed with dry benzene, and dried on porous tile in a vacuum (Found: Cl, 35.9.  $C_{12}H_{12}NCl_4As$  requires Cl, 36.7%).

The crystals formed above, on filtration in the ordinary manner, become opaque and then consist for the most part of diphenylamine hydrochloride. The same compound is produced when diphenylamine hydrochloride and arsenious chloride are mixed in the presence of a solvent.

In an experiment using arsenious chloride (20 g.), diphenylamine (17 g.) and *s*-tetrachloroethane (40 c.c.), the mixture was kept for 16 months. No change of pressure in the flask was observed. After making alkaline with sodium carbonate solution, the volatile products were distilled in steam. The residue (3.0 g.) was converted into 10-chloro-5:10-dihydrophenarsazine by treating it in hot acetic acid solution with dry hydrogen chloride. On cooling, the chloroarsine separated in greenish-yellow needles, m. p. 189—190°.

*p*-Phenylacetylaminophenylarsinic Acid (*N*-Acetyldiphenylamine-*p*-arsinic acid) (X).—A solution of *N*-acetyl-*p*-aminodiphenylamine (22.6 g.) in dilute hydrochloric acid (25 c.c. of concentrated acid and 150 c.c. of water) was cooled to 0° and diazotised with sodium nitrite (7.4 g.) in water (20 c.c.). The diazo-solution was added gradually, with vigorous stirring, to a solution of sodium arsenite made by dissolving arsenious oxide (15 g.) in sodium carbonate solution (24 g. of anhydrous sodium carbonate in 105 c.c. of water) containing a small amount of copper sulphate. The arsenite solution was maintained at 30—35° and kept alkaline by addition of sodium hydroxide solution. After the evolution of nitrogen had ceased, the solution was filtered from tarry matter and made slightly acid to litmus. This procedure caused a further quantity of dark-coloured, tarry matter to be precipitated. After filtration, and evaporation to small bulk, the crude acid (16.5 g.), m. p. 121°, was obtained by making the solution strongly acid. The pure acid, m. p. 126° (decomp.), crystallises from water in almost colour-

less prisms containing  $1\text{H}_2\text{O}$  (Found:  $\text{H}_2\text{O}$ , 4.7; As, 21.2.  $\text{C}_{14}\text{H}_{16}\text{O}_5\text{NAs}$  requires  $\text{H}_2\text{O}$ , 5.1; As, 21.2%).

*p*-Phenylaminophenylarsinic Acid (*Diphenylamine-p-arsinic acid*) (XII).—The crude acetyl-arsinic acid (15 g.) was boiled for one hour with a mixture of concentrated hydrochloric acid (30 c.c.) and alcohol (30 c.c.). The solution turned green and the required arsenic acid was precipitated by water. The crude acid (13 g.) contained some green matter very difficult to separate. Purification was conveniently accomplished by treating a concentrated solution of the ammonium salt with magnesium sulphate solution, when the sparingly soluble magnesium salt was precipitated. Extraction of the magnesium salt with successive quantities of hot water and treatment of the solution with dilute sulphuric acid resulted in the formation of almost colourless, hair-like crystals of the arsenic acid, m. p.  $265^\circ$  (decomp.) (Found: As, 25.5.  $\text{C}_{12}\text{H}_{12}\text{O}_3\text{NAs}$  requires As, 25.6%).

*p*-Phenylacetylaminophenylarsenious Chloride (*N-Acetyldiphenylamine-p-arsenious chloride*) (XI).—A hot solution of the acetyl-arsinic acid (9 g.) in alcohol (30 c.c.) and concentrated hydrochloric acid (9 c.c.) containing a trace of iodine was saturated with sulphur dioxide. On cooling, solid matter separated, and the mother-liquors on evaporation yielded a further crop of crystals. The *arsenious chloride*, after filtration and drying, crystallised from benzene-ligroin in colourless needles, m. p.  $141^\circ$  (Found: Cl, 20.0.  $\text{C}_{14}\text{H}_{12}\text{ONCl}_2\text{As}$  requires Cl, 20.0%).

Considerable difficulty has been met with in trying to prepare the arsenious chloride from *p*-phenylaminophenylarsinic acid. Attempts at reduction analogous to those of the corresponding acetyl derivative using the crude acid were unsuccessful owing to the persistence of the green matter. An attempt at reduction in the absence of hydrochloric acid to produce the oxide, caused elimination of the arsenic and diphenylamine was obtained, identified by its melting point and the melting point of its hydrochloride. The pure acid on reduction in the presence of hydrochloric acid gave a crystalline product which was mainly diphenylamine hydrochloride. The crystals did contain a small amount of a substance containing arsenic, but not in sufficient quantity for identification.

*Action of Arsenious Chloride on Aniline.*—Aniline (51 g.) was added carefully to arsenious chloride (18 g.), and the mixture boiled gently for 72 hours. During the heating a sublimate of aniline hydrochloride and ammonium chloride formed. The product was made alkaline with sodium hydroxide solution and steam-distilled until the distillate was free from aniline and ammonia. By continued steam distillation, diphenylamine, identified by its melting point and the melting point of its hydrochloride, was obtained.

The insoluble residue in the flask was filtered, washed with water, dried at 100°, and weighed (39% of theory). The crude oxy-compound was converted into 10-chloro-5:10-dihydrophenarsazine by hydrochloric acid and acetone, and subsequent evaporation of the solution to dryness. The crude chloro-compound on crystallisation from carbon tetrachloride melted at 186—187°.

*Action of Arsenious Chloride on  $\beta$ -Naphthylamine.*—A mixture of  $\beta$ -naphthylamine (21.5 g.), arsenious chloride (30 g.), and *o*-dichlorobenzene (60 c.c.) was boiled under reflux for 18 hours. On mixing, a colourless, crystalline compound separated, which on warming dissolved. Hydrogen chloride was evolved and a white solid (ammonium chloride) collected in the condenser. The solution, on cooling, deposited a dark orange, crystalline mass. This was purified by three crystallisations from nitrobenzene and was thus obtained in yellow needles, m. p. 355° (decomp.) (Found: As, 19.3; N, 3.9.  $C_{20}H_{13}NClAs$  requires As, 19.85; N, 3.7%).

*14-Chloro-14:7-dihydrodibenzophenarsazine (XIV).*—Di- $\beta$ -naphthylamine (13.5 g.), arsenious chloride (10 g.), and *s*-tetrachloroethane (70 c.c.) were boiled under reflux for 90 minutes. After the first 30 minutes the yellow product began to separate from the boiling solution. The compound was filtered off and crystallised from nitrobenzene, separating in yellow needles, m. p. 355° (decomp.). The yield was 55% of the theoretical (Found: As, 19.6; N, 3.9.  $C_{20}H_{13}NClAs$  requires As, 19.85; N, 3.7%).

*7-Chloro-7:14-dihydrodibenzophenarsazine (XV).*—Di- $\alpha$ -naphthylamine (13.5 g.; 1 mol.) and 10 g. of arsenious chloride (1.1 mols.) were boiled in 20 c.c. of *s*-tetrachloroethane for 7 hours. Hydrogen chloride escaped rather more slowly than in the previous preparations. The product separated, on cooling, as a brown powder (11.4 g., or 60.3%).

*7-Chloro-7:14-dihydrodibenzophenarsazine* crystallises from hot nitrobenzene in minute, yellowish-brown needles, m. p. 278—279° (decomp.) (Found: As, 19.6.  $C_{20}H_{13}NClAs$  requires As, 19.85%).

*10:10'-Oxy-5:10-dihydrophenarsazine.*—A mixture of diphenylamine (15 g.), arsenious oxide (2.9 g.), and phosphorus pentoxide (3.2 g.) is heated with vigorous mechanical stirring at 160—170° for 1 hour. On cooling, a hard, black cake is obtained which is treated with sodium carbonate solution, and steam-distilled, diphenylamine (10.7 g.) passing over. The remaining oxy-compound (5 g.) is filtered off, and converted into 10-chloro-5:10-dihydrophenarsazine by dissolving it in acetone by addition of sufficient hydrochloric acid and evaporating the resulting solution to dryness. Crystallisation from carbon tetrachloride gives the pure product.

A mixture of 10:10'-oxy-5:10-dihydrophenarsazine (10 g.),

acetyl chloride (3.2 g.) and dry benzene (100 c.c.) is boiled under reflux for 6 hours, solution occurring after a few minutes' heating; on cooling, crystalline matter separates. This is filtered off and on washing with cold acetone yields crude 10-chloro-5-acetyl-5:10-dihydrophenarsazine (3.5 g.), m. p. 221–224°. By crystallisation from benzene, the pure product is readily obtained (compare Burton and Gibson, *loc. cit.*).

If 10:10'-oxy-5:10-dihydrophenarsazine (19.1 g.) is treated with benzoyl chloride (10.7 g.; 2 mols.) under similar conditions, no 10-chloro-5-benzoyl-5:10-dihydrophenarsazine is produced, but 10-chloro-5:10-dihydrophenarsazine (20.5 g.; theory, 21.2 g.), m. p. 190–191°, and benzoic anhydride (7.9 g.; theory, 8.6 g.), m. p. 41°, are obtained.

*Molecular Compounds of 10-Chloro-5:10-dihydrophenarsazine.*—When 10-chloro-5:10-dihydrophenarsazine is crystallised from the following solvents, crystals are obtained containing solvent of crystallisation. These crystals effloresce slowly in air, but heating at 110° causes rapid dissociation, leaving pure 10-chloro-5:10-dihydrophenarsazine in each case.

(a) Acetic acid	A, C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	(Loss, 18.5; calc., 17.8%)
(b) <i>s</i> -Tetrachloroethane	2A, C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	{ „ 23.7; „ 23.2 }
(c) Chlorobenzene	2A, C <sub>6</sub> H <sub>5</sub> Cl	{ „ 17.0; „ 16.8 }
(d) <i>o</i> -Dichlorobenzene	2A, C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	{ „ 21.0; „ 20.9 }
(e) Acetone	2A, C <sub>3</sub> H <sub>6</sub> O	{ „ 9.3; „ 9.5 }
(f) Carbon tetrachloride	A, CCl <sub>4</sub>	{ „ 35.6; „ 35.7 }

(A denotes NH<C<sub>6</sub>H<sub>4</sub>>AsCl).

10-Chloro-5:10-dihydrophenarsazine is extremely soluble in arsenious chloride, giving a dark green solution. A hot, concentrated solution, on cooling, deposits magnificent, scarlet scales of the compound A, AsCl<sub>3</sub> (loss, 39.3; calc., 39.7%). This is sufficiently stable to allow of filtration, but on exposure to air or washing with solvents yields the original chloro-compound.

10-Bromo-5:10-dihydrophenarsazine.—(a) A mixture of diphenylamine (8.5 g.), arsenious bromide (17.3 g.), and *o*-dichlorobenzene (20 c.c.) is boiled under reflux for 18 hours. Hydrogen bromide is liberated steadily. The crude bromo-compound (9.6 g.) that separates on cooling crystallises from toluene in greenish-yellow prisms, m. p. 217–218°.

(b) 10-Acetyl-5:10-dihydrophenarsazine (15 g.) dissolved in boiling glacial acetic acid (200 c.c.) is treated with hydrobromic acid (10 c.c.; 30%) in glacial acetic acid (25 c.c.). On cooling, 10-bromo-5:10-dihydrophenarsazine (13.3 g.) separates (Found: As, 23.3; Br, 24.8%).

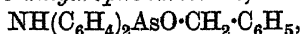
10-Iodo-5:10-dihydrophenarsazine.—On treating a hot solution

of 10-acetyl-5:10-dihydrophenarsazine (4.5 g.) in glacial acetic acid (70 c.c.) with hydriodic acid (2.5 c.c.; 50%) diluted with acetic acid (10 c.c.) the pure iodo-compound (5.6 g.) separates in brownish-orange needles, m. p. 217—221° (decomp.) (Found: As, 20.1%).

10-*n*-Butoxy-5:10-dihydrophenarsazine,  $\text{NH}(\text{C}_6\text{H}_4)_2\text{As}\cdot\text{O}\cdot\text{C}_4\text{H}_9$ .—A solution of 10:10'-oxy-5:10-dihydrophenarsazine (5 g.) in *n*-butyl alcohol (50 c.c.), on cooling deposited a mass of pale yellow needles, m. p. 158—160° (Found: As, 23.7.  $\text{C}_{16}\text{H}_{18}\text{ONAs}$  requires As, 23.8%).

A boiling solution of 10:10'-oxy-5:10-dihydrophenarsazine (15 g.) in *n*-butyl alcohol (180 c.c.) is saturated with dry hydrogen sulphide for 2 hours. The compound crystallises during the reaction and after collection is recrystallised from toluene. 10:10'-Sulpho-5:10-dihydrophenarsazine crystallises in yellow needles, m. p. 256—264° (decomp.). Yield 67% of theory (Found: As, 29.1%).

10-Benzoyloxy-5:10-dihydrophenarsazine,



prepared in an analogous manner to the corresponding *n*-butyl compound, crystallises in colourless needles, m. p. 173—175° (Found: As, 21.1.  $\text{C}_{19}\text{H}_{16}\text{ONAs}$  requires As, 21.5%).

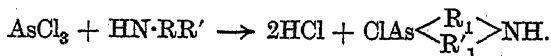
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## LIX.—10-Chloro-5:10-dihydrophenarsazine and its Derivatives. Part II. The Action of Primary Chloroarsines on Diphenylamine and its Homologues.

By HAROLD BURTON and CHARLES STANLEY GIBSON.

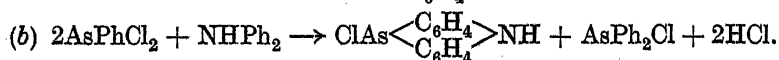
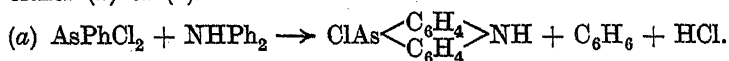
It has been shown (preceding paper) that the reaction between arsenious chloride and diphenylamine and its homologues goes very readily either when the two substances are heated alone, or more conveniently, in the presence of a suitable solvent, dihydrophenarsazine derivatives being formed. The reaction taking place may be generally expressed ( $\text{R}_1 = \text{R} - \text{H}$ ;  $\text{R}'_1 = \text{R}' - \text{H}$ ):



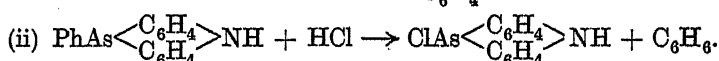
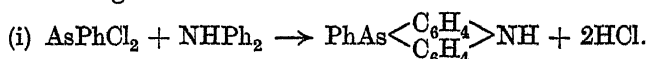
It seemed desirable to investigate the application of the reaction to the case of dichloroarsines with a view to obtain dihydrophenarsazine derivatives of the type  $\text{XAs} \begin{smallmatrix} \text{R}_1 \\ \text{R}'_1 \end{smallmatrix} \text{NH}$  [ $\text{X}$  = univalent hydrocarbon or substituted hydrocarbon radical]. The most

convenient dichloroarsine was phenyldichloroarsine, easily prepared by reducing phenylarsinic acid, which in turn is readily obtainable by the Bart reaction on aniline.

When the reaction between phenyldichloroarsine and diphenylamine was carried out under the conditions employed for preparing 10-chloro-5 : 10-dihydrophenarsazine, *viz.*, with equimolecular quantities heated in the presence of *o*-dichlorobenzene, the product was not 10-phenyl-5 : 10-dihydrophenarsazine, but 10-chloro-5 : 10-dihydrophenarsazine, the substance obtained by the condensation of arsenious chloride and diphenylamine. It appeared that the reaction to produce 10-chloro-5 : 10-dihydrophenarsazine might be either (a) or (b).



It was also recognised that reaction (a) might be the final result of the following two reactions.



In a preliminary experiment two molecules of the chloroarsine and one molecule of diphenylamine were heated together in *o*-dichlorobenzene solution. A theoretical yield of 10-chloro-5 : 10-dihydrophenarsazine calculated on the quantity of diphenylamine taken was obtained, and instead of the easily recognisable diphenylchloroarsine, only phenyldichloroarsine was obtained on examining the filtrate from the solid product. Experiments using molecular proportions of the reacting substances, heated for a longer time, also gave theoretical amounts of 10-chloro-5 : 10-dihydrophenarsazine, but it was not until the reaction was carried out in the absence of solvent that we were able to collect a volatile substance, which was identified as benzene.

In view of these results, the publication of a paper by Lewis and Stiegler (*J. Amer. Chem. Soc.*, 1925, 47, 2551) containing experiments on the condensation of  $\beta$ -chlorovinylchloroarsine with diphenylamine and phenyl- $\alpha$ -naphthylamine, and the description of the condensation products "6- $\beta$ -chlorovinylphenarsazine," and "7- $\beta$ -chlorovinyl-7 : 12-dihydro- $\gamma$ -benzophenarsazine," seemed somewhat anomalous to us, especially as the melting points of the two compounds quoted (186—187° and 213°, respectively) were so near to those of 10-chloro-5 : 10-dihydrophenarsazine and 7-chloro-

7:12-dihydrobenzophenarsazine (191—192° and 219—220°, respectively), and therefore we decided to repeat our work; extend it to other diarylamines; and finally repeat Lewis and Stiegler's experiments.

We have done this and find that our initial observations are correct. The extension of the work consisted in studying the action of phenyldichloroarsine on phenyl-*p*-tolylamine, *pp'*-ditolylamine, and phenyl- $\alpha$ -naphthylamine. In each case, the reaction proceeded as with diphenylamine and instead of the *As*-phenyl derivatives we obtained the chlorodihydrophenarsazine derivative.

The compound isolated from phenyl-*p*-tolylamine, namely, 10-chloro-2-methyl-5:10-dihydrophenarsazine,\* has been synthesised from the former substance and arsenious chloride. The *N*-acetyl derivative of this compound has been prepared, and also the corresponding *phenarsazinic acids*, using the method of Burton and Gibson (J., 1924, 125, 2276). The compound obtained from *pp'*-ditolylamine is referred to in the German Patent (D.R.-P. 281049, Friedländer, "Fortschritte," 1914, XII, 843), but so far as we can discover, this substance, 10-chloro-2:8-dimethyl-5:10-dihydrophenarsazine, has not yet been described in the literature. We have prepared it from *pp'*-ditolylamine and arsenious chloride, and also obtained its *N*-acetyl derivative.

A repetition of Lewis and Stiegler's work, adhering as far as possible to their quantities and conditions, showed that the reaction between diphenylamine and  $\beta$ -chlorovinyl-dichloroarsine proceeded in a similar manner to that using phenyldichloroarsine. In the presence of *o*-dichlorobenzene a quantitative yield of 10-chloro-5:10-dihydrophenarsazine was obtained, which after crystallisation from carbon tetrachloride melted at 186—187° and did not depress the melting point of a pure specimen. Further crystallisation from the same solvent gave a pure product, m. p. 190—191°, identical with an authentic specimen. From phenyl- $\alpha$ -naphthylamine in boiling *o*-dichlorobenzene solution we isolated 7-chloro-7:12-dihydrobenzophenarsazine, also in quantitative yield. In the absence of solvent, the yields were not so good, but the products obtained were identical with those from the experiments done in *o*-dichlorobenzene. It was found necessary to crystallise the crude 10-chloro-5:10-dihydrophenarsazine twice from carbon tetrachloride before it would melt at 190—191°, and although the product from phenyl- $\alpha$ -naphthylamine was crystallised from xylene, following Lewis and Stiegler's directions, it melted three degrees low, and had to be further crystallised from toluene before it was pure. We were able

\* The nomenclature of these compounds is described in the preceding paper.



to prove the formation of vinyl chloride in these experiments by passing the hydrogen chloride and vinyl chloride evolved through a solution of bromine in carbon tetrachloride, when the colour of the bromine was discharged. That this decoloration was not due to acetylene produced by decomposition of the  $\beta$ -chlorovinyl-dichloroarsine was further demonstrated by washing the carbon tetrachloride solution with dilute sodium carbonate solution, and after subsequent drying and removal of the carbon tetrachloride, determining the boiling point of the residue. This was  $160\text{--}162^\circ$ , which is in good agreement with the b. p.,  $162.5\text{--}163^\circ$ , recorded by Biltz (*Ber.*, 1902, 35, 3526) for  $\alpha$ -bromo- $\beta$ -chlorobromoethane.\* During these experiments we were unable to isolate any compound of the type  $\text{XAs} \begin{smallmatrix} \text{R}_1 \\ \text{R}_1 \end{smallmatrix} \text{NH}$ .

#### EXPERIMENTAL.

Freshly-made phenyldichloroarsine, b. p.  $247\text{--}250^\circ/752\text{ mm.}$ , and  $\beta$ -chlorovinyl-dichloroarsine, b. p.  $93\text{--}94^\circ/24\text{ mm.}$ , were used in the following experiments. The diphenylamine and *o*-dichlorobenzene also were freshly distilled.

*Condensations of Phenyldichloroarsine with Diphenylamine and Related Compounds.*—(a) *In the presence of solvent.* In the preliminary experiments a mixture of diphenylamine (8.45 g.), phenyldichloroarsine (22.3 g.), and *o*-dichlorobenzene (20 c.c.) was heated under reflux for 8 hours. Hydrogen chloride had then ceased to be evolved. The green solution was cooled, mixed with petrol (20 c.c.), and the solid filtered off. This, after being washed with petrol (30 c.c.) and dried to constant weight at  $100^\circ$ , crystallised from benzene in yellow needles, m. p.  $189\text{--}190^\circ$ , and was identical in all respects with an authentic sample of 10-chloro-5:10-dihydrophenarsazine prepared from diphenylamine and arsenious chloride. The yield was almost theoretical.

Similar experiments using (a) phenyl-*p*-tolylamine, (b) di-*p*-tolylamine, and (c) phenyl- $\alpha$ -naphthylamine gave (a) 10-chloro-2-methyl-5:10-dihydrophenarsazine, m. p.  $199\text{--}200^\circ$  (decomp.), (b) 10-chloro-2:8-dimethyl-5:10-dihydrophenarsazine, m. p.  $261\text{--}262^\circ$ , after

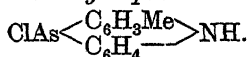
\* Lewis and Stiegler, in calculating the value for the percentage of chlorine in the supposed 10- $\beta$ -chlorovinyl-5:10-dihydrophenarsazine, arrived at too high a value, the actual figure being 11.69% instead of 12.00%. Their low analytical data for a sample of pure 10-chloro-5:10-dihydrophenarsazine together with its low melting point explain, in all probability, the reason they have assigned the wrong constitution to this compound. The obvious impurity of their 7-chloro-7:12-dihydrobenzophenarsazine, the m. p. of which was  $6^\circ$  below that of a pure specimen, is, no doubt, the cause of their low analytical data.

previous decomposition, and (c) 7-chloro-7:12-dihydrobenzophenarsazine, m. p. 218—219°.

In the second series of experiments, half the quantity of phenyldichloroarsine was used and the mixture was boiled for 16 hours. The product was treated in the same manner, and a yield of 93% of the theoretical quantity of 10-chloro-5:10-dihydrophenarsazine was obtained. (The yields of the other chlorodihydrophenarsazines varied from 90—95%.)

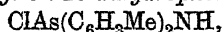
(b) *In the absence of solvent.* These experiments consisted in heating mixtures of diphenylamine and phenyldichloroarsine, in the molecular ratio of 1:1 and 1:2, in a metal-bath, the temperature of which was raised to 230° during 30 minutes and maintained for 45 minutes. The volatile product, after being washed with dilute sodium carbonate solution and dried, boiled at 80°; it was benzene. The residue in the flask, after crystallising from boiling *o*-dichlorobenzene, was 10-chloro-5:10-dihydrophenarsazine.

10-Chloro-2-methyl-5:10-dihydrophenarsazine,



—A mixture of phenyl-*p*-tolylamine (36.6 g.), arsenious chloride (40 g.), and *o*-dichlorobenzene (80 c.c.) was boiled under reflux for 4 hours. On cooling, the chloro-compound (51 g.) separated as a mass of green crystals. On crystallisation from benzene, the substance was obtained in yellow needles, m. p. 199—200° (decomp.) (Found: Cl, 12.3.  $\text{C}_{13}\text{H}_{11}\text{NClAs}$  requires Cl, 12.2%).

10-Chloro-2:8-dimethyl-5:10-dihydrophenarsazine,



was prepared by heating together for 4 hours a mixture of di-*p*-tolylamine (32.7 g.), arsenious chloride (33.2 g.), and *o*-dichlorobenzene (133 c.c.). The crude chloro-compound (44.7 g.) crystallised from nitrobenzene in orange prisms, m. p. 261—262° with previous decomposition (compare D.R.-P., *loc. cit.*) (Found: As, 24.2.  $\text{C}_{14}\text{H}_{13}\text{NClAs}$  requires As, 24.5%).

10-Chloro-5-acetyl-2-methyl-5:10-dihydrophenarsazine was prepared by boiling a mixture of the corresponding phenarsazine (30 g.) with acetic anhydride (60 c.c.) for 3½ hours. On cooling, the *acetyl* derivative (25 g.) separated in almost colourless crystals. It separated from benzene-light petroleum in clusters of almost colourless needles, m. p. 154—155° (Found: Cl, 10.7.  $\text{C}_{15}\text{H}_{13}\text{ONClAs}$  requires Cl, 10.6%).

10-Chloro-5-acetyl-2:8-dimethyl-5:10-dihydrophenarsazine.—A suspension of the chloroarsine (10 g.) in acetic anhydride (50 c.c.) was boiled for 2 hours, when solution was complete and the colour of

the original compound had almost disappeared. After removal of half the acetic anhydride by distillation the crude acetyl compound separated in nearly colourless needles. It separated from benzene-light petroleum in colourless needles, m. p. 164—165° (Found: As, 21.4.  $C_{16}H_{15}ONClAs$  requires As, 21.6%).

*2-Methylphenarsazinic acid*,  $NH\langle\begin{smallmatrix} C_6H_3Me \\ C_6H_4 \end{smallmatrix}\rangle AsO.OH$ , separated in good yield when a mixture of the chloroarsine and chloramine-T had stood for 12 hours. It crystallised from aqueous acetic acid in colourless, fine needles which did not melt when heated but decomposed above 300° (Found: As, 25.6.  $C_{13}H_{12}O_2NAs$  requires As, 25.9%). The *sodium* salt crystallises from water in colourless, hair-like needles. The *hydrochloride* was obtained by treating a suspension of the acid in boiling alcohol with concentrated hydrochloric acid until crystalline matter began to separate. On cooling, the hydrochloride separated in colourless, small prisms, m. p. 209—211° (decomp.) (Found: Cl, 10.9.  $C_{13}H_{12}O_2NAs.HCl$  requires Cl, 10.9%).

*2:8-Dimethylphenarsazinic acid* was prepared by boiling a suspension of the chloroarsine (10 g.) in acetone (200 c.c.) with a solution of chloramine-T (18.5 g. in 185 c.c. of water) for 30 minutes. The orange colour of the original substance disappeared and colourless, crystalline matter was produced. The *acid* (6.3 g.) separated from aqueous acetic acid in colourless, glistening plates, which decomposed without melting at a high temperature (Found: As, 24.5.  $C_{14}H_{14}O_2NAs$  requires As, 24.7%). The *sodium* salt crystallises from water in colourless needles, and the *hydrochloride*, prepared as above, was obtained in colourless needles, m. p. 216° (decomp.) after previous softening (Found: As, 21.7.  $C_{14}H_{14}O_2NAs.HCl$  requires As, 22.1%).

*N-Acetyl-2:8-dimethylphenarsazinic acid*, prepared in the usual manner, separated from dilute acetic acid in colourless prisms, m. p. 240° (decomp.) (Found: As, 21.65.  $C_{15}H_{16}O_3NAs$  requires As, 21.7%).

*Condensation of  $\beta$ -Chlorovinylchloroarsine with Diphenylamine and Phenyl- $\alpha$ -naphthylamine.*—(a) *In the presence of solvent.* The mixture of diphenylamine (10.6 g.),  $\beta$ -chlorovinylchloroarsine (13.0 g.), and *o*-dichlorobenzene (25 c.c.) was boiled under reflux for 12 hours. Owing to the formation of a certain amount of tarry matter, the crude compound, isolated as in the phenylchloroarsine experiments, was extracted in a Soxhlet with carbon tetrachloride. The 10-chloro-5:10-dihydrophenarsazine obtained melted at 187° without further crystallisation, and a sample of it did not depress

the melting point of an authentic specimen. The yield was quantitative. Further crystallisation from the same solvent gave pure 10-chloro-5:10-dihydrophenarsazine, m. p. 190—191°. A similar experiment using phenyl- $\alpha$ -naphthylamine gave 7-chloro-7:12-dihydrobenzophenarsazine, m. p. 218—219°.

(b) *In the absence of solvent.* The quantities and conditions used in these experiments were the same as those described by Lewis and Stiegler. The only difference in procedure after the initial reaction was that the crude mass from the diphenylamine was extracted with carbon tetrachloride in a Soxhlet apparatus and finally crystallised from carbon tetrachloride. In this way, we obtained a specimen of pure 10-chloro-5:10-dihydrophenarsazine, m. p. 190—191° (Found: Cl, 12.8; As, 26.8%). From the phenyl- $\alpha$ -naphthylamine experiment pure 7-chloro-7:12-dihydrobenzophenarsazine was obtained, m. p. 219—220° (compare Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218) after a further crystallisation from toluene (Found: Cl, 10.9%).

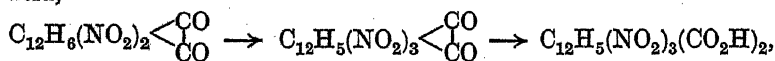
GUY'S HOSPITAL MEDICAL SCHOOL,  
LONDON, S.E. 1.

[Received, January 4th, 1926.]

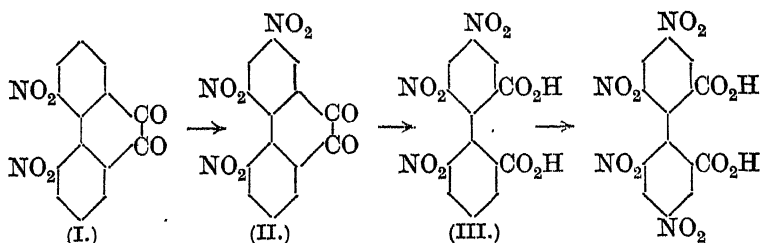
# LX.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part V. The Identity of the Nitration Products derived from 2:7- and 4:5-Dinitrophenanthraquinones.*

By GEORGE HALLATT CHRISTIE and JAMES KENNER.

THE conversion of 2:7-dinitrophenanthraquinone successively into 2:4:7-trinitrophenanthraquinone and 4:6:4'-trinitrodiphenic acid,



has been already described (Christie and Kenner, *J.*, 1923, **123**, 779). At the same time, it was intimated that a similar set of reactions had been carried out in the case of the dinitro-quinone which is produced with the 2:7-isomeride by nitration of phenanthraquinone and which Schmidt and Kämpf (*Ber.*, 1903, **36**, 3745) concluded to be a 4:5-derivative (I). The new trinitro-quinone was therefore thought to be a 2:4:5-derivative (II), and so different from the above-mentioned 2:4:7-isomeride, when it was oxidised to a diphenic acid (III) from which 4:6:4':6'-tetra-nitrodiphenic acid was obtained by further nitration:



It was therefore remarkable that when the acid (III) was resolved into optically active forms by fractional crystallisation of the quinidine or, better, of the quinine salts, a very close correspondence was revealed between the physical constants of the various salts and of those derived from the 4 : 6 : 4'-trinitro-acid. This will be apparent from the following table :

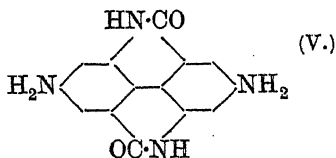
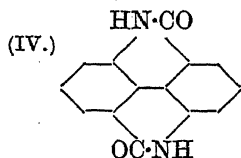
	4 : 6 : 4'-Acid. 289—290°	New acid. 291°
Melting point.		
Quinine <i>d</i> -salt.	M. p. 222°; $[\alpha]_D -156.4^\circ$	M. p. 222°; $[\alpha]_D -156.1^\circ$
„ <i>l</i> -salt.	M. p. 175°; $[\alpha]_D -69.1^\circ$	M. p. 176°; $[\alpha]_D -77.5^\circ$
Quinidine <i>l</i> -salt.	M. p. 229°; $[\alpha]_D -191.1^\circ$	M. p. 228°; $[\alpha]_D -189.2^\circ$
„ <i>d</i> -salt.	M. p. 176°; $[\alpha]_D 85.5^\circ$	M. p. 178°; $[\alpha]_D 109.9^\circ$
Sodium salt, <i>d</i> -acid.	$[\alpha]_D -152.3^\circ$	$[\alpha]_D -151.1^\circ$

This agreement also extends to the original trinitro-quinones, each of which crystallises from benzene in yellow, hexagonal prisms, which melt at 209° and contain one molecular proportion of benzene of crystallisation.

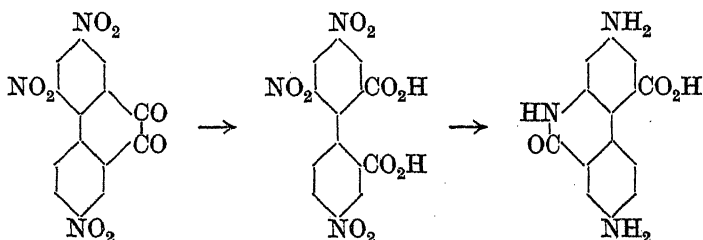
In spite, therefore, of the apparently conclusive nature of the evidence in favour of the constitutional formulæ assigned to these various compounds, the possibility suggested itself that the two series might in reality be identical. This was confirmed when it was found that the melting point of the two acids was not depressed by mixing them, and that the same applied to the *quinoxaline* derivative, m. p. 307°, prepared by condensing each of the trinitro-quinones with *o*-phenylenediamine. It followed either that the orientation of the two dinitro-quinones, from which the same trinitro-quinone had been obtained, was in some respect faulty or that, in the course of nitration of these dinitro-compounds, migration of a nitro-group had occurred in one case. Whichever of these be correct, it seemed advisable if possible to determine the orientation of the trinitro-compound by an independent method.

It had previously been shown (Kenner and Stubbings, J., 1921, 119, 593) that  $\gamma$ -6 : 6'-dinitrodiphenic acid was converted by reduction into a phenanthridone derivative (IV), and it was now found that 4 : 6 : 4' : 6'-tetranitrodiphenic acid is similarly convertible

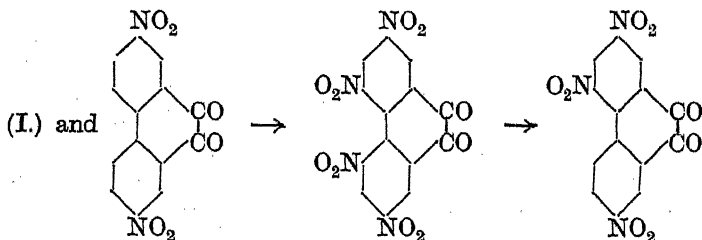
into the corresponding diamino-compound (V), of which both neutral and basic sulphates were isolated.



The trinitrodiphenic acid, however, under similar conditions yielded an amino-acid soluble both in alkali and in excess of mineral acid. Clearly this result indicates that the trinitro-acid is a 4:6:4'-derivative, derived from a 2:4:7-trinitrophenanthraquinone:

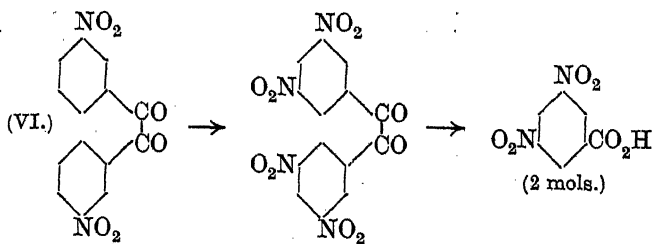


It has been pointed out (J., 1923, **123**, 780) that a 2:4:5:7-tetra-nitrophenanthraquinone could not be obtained from the trinitro-compound under very vigorous conditions of nitration. Hence it was just conceivable that the production of the same trinitro-compound from the two dinitrophenanthraquinones was due to the formation of the tetranitro-derivative in the first place, followed by elimination of a nitro-group under the conditions of experiment:



Although this would be a novel reaction, and is not observed in the case of the compound 4:6:4':6'-tetranitrodiphenic acid, it was deemed advisable to examine the behaviour of the closely related compound, 3:3'-dinitrobenzil (VI), on nitration. No difficulty was experienced in converting this into the corresponding

3:5:3':5'-tetranitrobenzil, the constitution of which was proved by its oxidation to 3:5-dinitrobenzoic acid:



### EXPERIMENTAL.

*2:4:7-Trinitrophenanthraquinone from 4:5-Dinitrophenanthraquinone.*—When the procedure described in the case of 2:7-dinitrophenanthraquinone (Christie and Kenner, *loc. cit.*, p. 783) was applied to the 4:5-isomeride, the trinitro-derivative was obtained, after crystallisation from benzene, in stout, yellow prisms, m. p. 209° (Found: loss of weight at 120°, 18.6.  $C_{14}H_5O_8N_3 \cdot C_6H_6$  requires loss, 18.5%. Found for material previously heated at 120°. N, 12.3.  $C_{14}H_5O_8N_3$  requires N, 12.25%). Solutions of the quinone (0.75 g.) and *o*-phenylenediamine (0.38 g.) in glacial acetic acid reacted at once when mixed. The precipitated quinoxaline derivative separated from benzene in clusters of colourless needles, m. p. 307° (Found: N, 16.75.  $C_{20}H_9O_8N_5$  requires N, 16.9%). An identical product was obtained from the quinone derived from 2:7-dinitrophenanthraquinone.

*4:6:4'-Trinitrodiphenic Acid from 4:5-Dinitrophenanthraquinone.*—The acid prepared from the above trinitroquinone by the usual process of oxidation with potassium dichromate and sulphuric acid was obtained first as an oil and then as a solid, m. p. 292° [Found: equiv., 188.3.  $C_{12}H_5O_6N_3(CO_2H)_2$  requires equiv., 188.5]. Solutions of the acid (4.6 g.) in alcohol (100 c.c.) and of quinine hydrate (9.2 g.) in alcohol (70 c.c.) were mixed and boiled; a salt (5.8 g.) separated on cooling. On evaporating the alcoholic liquor, an oil remained from which a second salt (5.8 g.) was obtained by treatment with dry ether.

*Quinine d-4:6:4'-trinitrodiphenate*, the less soluble of the two salts so obtained, forms colourless, octahedral prisms, m. p. 222.5° (decomp.) and free from alcohol. For a 1.25% solution in 10*N*-acetic acid,  $[\alpha]_D^{25} = -156.1^\circ$  (Found: N, 9.6.  $C_{34}H_{55}O_{14}N_7$  requires N, 9.6%).

*Quinine l-4:6:4'-trinitrodiphenate* melts at 176° (decomp.) after repeated purification by solution in alcohol and precipitation by

ether. For a 0.5% solution in chloroform,  $[\alpha]_D^{20} = -77.5^\circ$  (Found: N, 9.7.  $C_{54}H_{55}O_{14}N_7$  requires N, 9.6%).

Quinidine salts, m. p.  $228^\circ$  and  $178^\circ$ , agreeing in crystalline form with those previously described (Christie and Kenner, *loc. cit.*) were also obtained. For 0.7% solutions in chloroform, the respective observed values for  $[\alpha]_D$  were  $-189.2^\circ$  and  $+109.9^\circ$ . The poor agreement between the latter value and that previously recorded is to be attributed partly to a clerical error, which led to the value  $56.04^\circ$  being quoted in place of the correct value of  $85.55^\circ$ , and partly to the lower melting point of the salt employed on the previous occasion.

*d*-4 : 6 : 4'-Trinitrodiphenic acid, prepared from the quinine salt in the manner described in the earlier papers, was an oil which very slowly solidified to colourless prisms, m. p.  $281-282^\circ$  (decomp.). For a 3.11% solution in ether,  $[\alpha]_D = +23.47^\circ$ , and on conversion into a 1.48% solution of the sodium salt,  $[\alpha]_D = -149.0^\circ$ . For a 0.84% solution of sodium salt prepared without investigating the rotatory power of the acid,  $[\alpha]_D = -151.1^\circ$ . For a 1.36% solution of the sodium salt from the quinidine salt, m. p.  $178^\circ$ ,  $[\alpha]_D = -146.1^\circ$ , and the acid melted at  $281-282^\circ$  (decomp.).

*l*-4 : 6 : 4'-Trinitrodiphenic acid, from the quinine salt, melted and decomposed at  $280-282^\circ$ , and showed  $[\alpha]_D = -15.14^\circ$  for a 2.80% solution in ether. For a 1.05% solution of the sodium salt subsequently prepared,  $[\alpha]_D = +136.6^\circ$ . The changes in sign of rotatory power thus observed in passing from the acid to the sodium salt show that the prefixes *d*- and *l*- as used in the previous paper require to be interchanged.

Quinine salts prepared from the acid derived from 2 : 7-dinitrophenanthraquinone melted at  $222^\circ$  and  $175^\circ$ , respectively, and exhibited specific rotatory powers of  $-156.4^\circ$  (1.28% solution in 10*N*-acetic acid) and  $-69.11^\circ$  (0.63% solution in chloroform).

*Reduction of 4 : 6 : 4' : 6'-Tetranitrodiphenic Acid.*—When a solution of stannous chloride (33 g.) in hydrochloric acid (30 c.c.) was slowly added to a solution of the acid (3 g.) in glacial acetic acid (30 c.c.) and hydrochloric acid (24 c.c.), heat was evolved, a red colour was produced which slowly disappeared, and a precipitate formed. This was collected after the mixture had been boiled for an hour, and after being washed with hydrochloric acid it was dissolved in concentrated sulphuric acid. By cautious dilution with water, yellow plates were obtained which turned green when exposed to the air and light, and left no residue on ignition. They blackened, but did not melt, when heated to  $300^\circ$  (Found: N, 15.2.  $C_{14}H_{10}O_2N_4 \cdot H_2SO_4$  requires N, 15.4%). The aqueous extract obtained by warming the material with sodium carbonate



solution was shown in the usual manner to contain sulphate ions.

When a solution of the material in sulphuric acid was added to sodium acetate solution, a green precipitate was obtained which still contained sulphur after being thoroughly washed and was apparently a basic sulphate (Found: N, 17.7.  $C_{14}H_{10}O_2N_4 \cdot \frac{1}{2}H_2SO_4$  requires N, 17.8%).

*Reduction of 4:6:4'-Trinitrodiphenic Acid.*—The result of applying the procedure described above to 4:6:4'-trinitrodiphenic acid was less satisfactory than that of heating a suspension of the finely ground acid in hydrochloric acid at 100° with an amount of tin about 50% in excess of that theoretically necessary for complete reduction. By collecting the almost colourless solid portion of the product, washing it with hydrochloric acid, and cautious precipitation with water of its solution in sulphuric acid, a yellow material was obtained which turned green on exposure to air and exhibited the properties of an amino-acid [Found: N, 11.3; equiv., 120.6.  $C_{13}H_{10}ON_3(CO_2H) \cdot H_2SO_4$  requires N, 11.45%; equiv., 122.3].

*3:5:3':5'-Tetranitrobenzil.*—Dinitrobenzil (30 g.) reacted vigorously with nitric acid (150 g.;  $d$  1.5) and sulphuric acid (180 g.) when heated at 100° for 10 minutes, so that it was necessary to cool the liquid. Finally, the mixture was heated for 20 hours at 100° and then poured on to ice. The solid product consisted of 3:5-dinitrobenzoic acid (m. p. 205°, equiv. 213.1) and a neutral substance insoluble in cold sodium carbonate solution. By crystallisation from benzene, yellow needles of a tetranitrobenzil, m. p. 168°, were obtained (Found: N, 14.35.  $C_{14}H_6O_{10}N_4$  requires N, 14.35%). Its orientation was demonstrated by adding excess of hydrogen peroxide to a solution of the compound in dilute aqueous sodium hydroxide. Heat was evolved and after about  $\frac{1}{2}$  hour the dark coloration first produced had given place to a pale yellow. An excellent yield of 3:5-dinitrobenzoic acid was obtained on acidification. Tetranitrobenzil was, however, unchanged by prolonged heating with the above nitration mixture, so that it was not an intermediate product in the formation of dinitrobenzoic acid from dinitrobenzil.

The *quinoxaline* derivative of tetranitrobenzil, prepared in the usual manner by condensation in glacial acetic acid solution, formed colourless needles, m. p. 274° (Found: N, 18.4.  $C_{20}H_{10}O_8N_6$  requires N, 18.2%).

One of us (G. H. C.) wishes to make grateful acknowledgment of a grant from the Department of Scientific and Industrial Research

which enabled him to participate in this work. We are also indebted to the Research Fund Committee of the Chemical Society for a grant towards the purchase of materials.

THE UNIVERSITY, SHEFFIELD.

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## LXI.—Orientation Effects in the Diphenyl Series. Part I.

By HENRY GEORGE DENNETT and EUSTACE EBENEZER TURNER.

SINCE the nitration of 4 : 4'-dihydroxydiphenyl (Kunze, *Ber.*, 1888, 21, 3331; Schultz, *ibid.*, 3530; Hirsch, *ibid.*, 1889, 22, 336) and of its diethyl ether (Hirsch, *loc. cit.*; Brady and McHugh, *J.*, 1923, 123, 2047) affords symmetrical (3 : 5'-)dinitro-derivatives, it might be supposed that 4 : 4'-dibromodiphenyl would nitrate to give 4 : 4'-dibromo-3 : 5'(or 3 : 3')-dinitrodiphenyl. Unsymmetrical nitration, however, actually occurs, with the almost quantitative formation of the 2 : 3'(2 : 5'?)-dinitro-compound. This is the first example of unsymmetrical substitution in the diphenyl series.

Whilst the nitration of *p*-tolyl ethyl ether apparently affords only the 3-nitro-derivative (Staedel, *Annalen*, 1883, 217, 162), *p*-chlorotoluene yields a mixture of approximately equal quantities of the 2- and 3-nitro-compounds (Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 257).

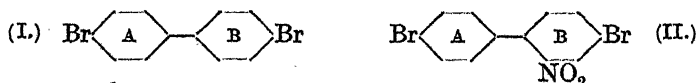
The nitration of 4 : 4'-dibromodiphenyl was described by Fittig (*Annalen*, 1864, 132, 206) and Schultz (*ibid.*, 1874, 174, 218) as giving a dinitro-derivative, m. p. 148°, regarded by Beilstein (*Handbuch*, 4th Edn., v, 585) as probably being identical with the 2 : 2'-dinitro-compound, m. p. 138°, previously synthesised by Ullmann and Bielecki (*Ber.*, 1901, 34, 2177). The work of Fittig and Schultz has been repeated and confirmed. Reduction of their dinitro-compound afforded the diamine, m. p. 89°, described by Schultz (*loc. cit.*), but this diamine could not be caused to undergo condensations of the type to be expected of a symmetrical diamine. This appeared to show that unsymmetrical nitration had occurred. Moreover, the dinitro-derivative depressed the m. p. of the 2 : 2'-dinitro-compound obtained from 2 : 5-dibromonitrobenzene (Ullmann and Bielecki, *loc. cit.*).

4 : 4'-Dibromo-2-nitrodiphenyl, prepared from 2-nitrobenzidine, was identical with the mononitro-derivative, m. p. 124°, prepared by Lellmann's method (*Ber.*, 1882, 15, 2837) and apparently is the first product of nitration of dibromodiphenyl. When nitrated, it was converted into the dinitro-compound, m. p. 148°, which there-

fore has one nitro-group in position 2. It was then found that one bromine atom in the dinitro-compound possessed much greater reactivity than the other.

Hot, concentrated potassium hydroxide had no action on the dinitro-compound, which, however, reacted vigorously with piperidine to give a bromopiperidinodinitrodiphenyl. 4:4'-Dibromo-2-nitrodiphenyl and 4:4'-dibromo-2:2'-dinitrodiphenyl were not affected by piperidine, and it is therefore clear that the above piperidino-derivative is 4-bromo-4'-piperidino-2:3'-dinitrodiphenyl, and that the original dinitro-compound is the 2:3'-derivative.\*

In the entrance of a nitro-group into the B nucleus of dibromodiphenyl (I), the bromophenyl group A apparently has greater directive influence than the bromine atom in B, the nitro-group



entering position 2, whilst in the nitration of the mononitro-compound (II), conditions are favourable, according to the ordinary theories of substitution, for 3'-nitration in A.

It has similarly been found that the dinitro-derivative of 4:4'-dichlorodiphenyl described by Schmidt and Schultz (*Annalen*, 1881, 207, 340) is 4:4'-dichloro-2:3'-dinitrodiphenyl. It reacts with piperidine even more readily than does the corresponding dibromocompound, giving 4-chloro-4'-piperidino-2:3'-dinitrodiphenyl. The relative activation, by a nitro-group, of a chlorine and a bromine atom is a subject it is hoped to investigate later on.

The diamine referred to above is therefore 4:4'-dibromo-2:3'-diaminodiphenyl. Schultz (*loc. cit.*), by oxidising this substance, obtained what he called a bromaminobenzoic acid, m. p. 155°. This was probably a mixture of 4-bromo-2-amino- and 4-bromo-3-amino-benzoic acids, which melt respectively at 225° and 222°. Further, Strasser and Schultz (*Annalen*, 1881, 210, 194), by reducing, and thus debrominating, the diamine, obtained a base which they called  $\gamma$ -benzidine. This is evidently 2:3'-diaminodiphenyl.

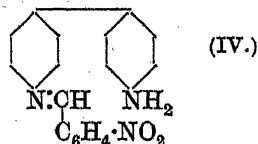
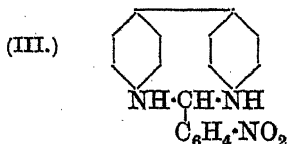
A preliminary investigation has shown that the nitration of 4:4'-ditolyl affords, first, a mononitro-compound, m. p. 91–92°,

\* It might be objected that in the nitration of dibromodiphenyl, both nitro-groups could enter the same nucleus. Against this objection, however, are at least three facts: (1) the difficulty of introducing a third substituent into one nucleus of diphenyl compounds other than hydroxy- and amino-derivatives, (2) the reactivity of one bromine atom in the dinitro-compound, which, if nitration occurred twice in the same nucleus, would almost certainly be 4:4'-dibromo-2:6-dinitrodiphenyl, i.e., a compound containing no reactive bromine atom, and (3) the quantitative nature of the nitration.

and then a dinitro-compound, m. p.  $119^{\circ}$ . The latter we regard as the 2:3'-dinitro-compound. Ullmann and Frentzel (*Ber.*, 1905, 38, 726) have described the 3:3'(3:5'?)-derivative, which for present purposes has been prepared by heating 4-iodo-2-nitrotoluene with copper bronze.

The preparation of compounds containing amino-groups in the 3:3'- or 3:5'-positions in the diphenyl molecule is a matter of considerable difficulty. According to Ullmann and Frentzel (*loc. cit.*), when *m*-nitrobenzenediazonium sulphate is added, under certain conditions, to cuprous chloride and hydrochloric acid, the chief product is 3:3'(3:5'?)-dinitrodiphenyl. We have found, on the contrary, that excellent yields of *m*-chloronitrobenzene are invariably obtained (compare Emde, *Apoth. Ztg.*, 1915, 30, 293). The dinitro-compound may be obtained from *m*-iodonitrobenzene as stated by Ullmann and Bielecki (*loc. cit.*). The latter substance is only obtainable in small yields by the method of Jacobson, Fertsch, and Heubach (*Annalen*, 1898, 303, 338), but this difficulty has now been overcome.

During some experiments on the condensation of aldehydes with benzidine, we prepared from *p*-nitrobenzaldehyde a compound to which Barzilowski (*J. Russ. Phys. Chem. Soc.*, 1891, 23, 69) had assigned formula (III). We have found that this compound readily condenses with a second molecule of a keto-compound, and is therefore (IV).



#### EXPERIMENTAL.

*Nitration of 4:4'-Dibromodiphenyl.*—Nitration in glacial acetic acid by Lellmann's method (*loc. cit.*) gave a mononitro-compound, m. p.  $124^{\circ}$ . Nitration using excess of nitric acid (*d* 1.5) gave a crude dinitro-compound, m. p.  $130\text{--}135^{\circ}$ , which, after being once crystallised from benzene, melted at  $148^{\circ}$ . A small quantity of the mononitro-compound was obtained from the mother-liquors.

The dinitro-compound was not affected when boiled with very concentrated aqueous potassium hydroxide, whilst alcoholic alkali led to a black product which will be investigated in due course.

*Preparation of 4:4'-Dibromo-2-nitrodiphenyl.*—2-Nitrobenzidine sulphate was ground into a fine paste with a little water and diazotised at  $5^{\circ}$ . The solution was poured with vigorous shaking into a cold suspension of cuprous bromide in hydrobromic acid-sodium

bromide. The vigorous reaction over, the whole was heated at 100° for a short time and the gummy solid was collected and warmed with sodium hydroxide to remove phenolic substances. The yellow residue, containing considerable quantities of benzerythrene derivatives, after several crystallisations from alcohol and benzene, melted at 124°. The m. p. was not affected by admixture with the first-named nitro-compound (Found: Br, 4.5.  $C_{12}H_7O_2NBr_2$  requires Br, 4.5%).

*Nitration of 4:4'-Dibromo-2-nitrodiphenyl.*—This substance was dissolved in two parts of warm nitric acid ( $d$  1.5). On cooling, pale yellow needles separated, which, after crystallisation from benzene, melted at 148° and did not depress the m. p. of the above dinitro-compound having the same m. p.

*4-Bromo-4'-piperidino-2:3'-dinitrodiphenyl.*—The dinitro-compound, m. p. 148°, was gently warmed with a little piperidine for about a minute. An orange colour at once developed, and, on cooling, the whole set to a crystalline paste owing to the separation of piperidine hydrobromide. It was treated with water, and the orange-red solid so obtained once crystallised from alcohol; the *piperidino*-compound was then obtained in orange-red needles, m. p. 136—137° (Found: Br, 19.3.  $C_{17}H_{16}O_4N_3Br$  requires Br, 19.7%). The *piperidino*-compound was unaffected by further heating with piperidine.

4:4'-Dibromo-2-nitro- and 4:4'-dibromo-2:2'-dinitro-diphenyl were also heated for several minutes with piperidine. In both cases the compounds were recovered unchanged.

*Preparation of 4:4'-Dibromo-2:3'-diaminodiphenyl.*—The corresponding dinitro-compound was reduced with iron, water, and ferric chloride (Roberts and Turner, J., 1925, 127, 2004). The properties of the diamine agreed with those recorded in the literature. It condensed with salicylaldehyde, but not with carbon disulphide, under conditions similar to those under which benzidine readily condenses with this substance.

*Disalicylidene-4:4'-dibromo-2:3'-diaminodiphenyl* separates from benzene as a yellow, crystalline powder, m. p. 195° (Found: N, 5.1.  $C_{28}H_{18}O_2N_2Br_2$  requires N, 5.1%).

*Nitration of 4:4'-Dichlorodiphenyl.*—The dichloro-compound readily dissolved in warm nitric acid ( $d$  1.5), and, on cooling, the dinitro-compound crystallised out. After washing and drying, it was once crystallised from alcohol and then had m. p. 140°.

*4-Chloro-4'-piperidino-2:3'-dinitrodiphenyl.*—The dichloro-compound was warmed for a few seconds with piperidine, the mixture diluted, and the product filtered off, washed with water, and crystallised from alcohol; the *piperidino*-compound was then obtained in

orange needles, m. p.  $132^{\circ}$  (Found: Cl, 10.0.  $C_{17}H_{16}O_4N_3Cl$  requires Cl, 9.8%). The piperidino-compound was not affected by further heating with piperidine, which also had no effect on 4:4'-dichloro-2:2'-dinitrodiphenyl prepared from 2:5-dichloronitrobenzene by the method of Ullmann and Bielecki (*loc. cit.*).

*Preparation of Mononitro-4:4'-ditolyl.*—A solution of ditolyl in glacial acetic acid containing one equivalent of nitric acid ( $d$  1.4) was evaporated until, on cooling, yellow prisms separated. These, after crystallisation from alcohol, melted at  $91$ – $92^{\circ}$  (Found: N, 6.2.  $C_{14}H_{13}O_2N$  requires N, 6.1%). The nitro-compound is readily soluble in alcohol, acetic acid, or benzene. Ditolyl is unaffected when dissolved in cold acetic-nitric acid mixtures.

*Preparation of Dinitro-4:4'-ditolyl.*—Sufficient nitric acid ( $d$  1.5) was added to the hydrocarbon to form a clear solution, without cooling. On leaving, slender, yellow needles separated. These, after being collected, washed with water, and crystallised from alcohol, and then from glacial acetic acid, melted at  $119^{\circ}$  (Found: N, 10.6.  $C_{14}H_{12}O_4N_2$  requires N, 10.3%).

*Preparation of 3:3' (3:5')-Dinitro-4:4'-ditolyl.*—4-Iodo-2-nitrotoluene was prepared from 2-nitro-*p*-toluidine as follows: the base (30 g.) was diazotised in dilute sulphuric acid, and the product added to a cold and well-shaken solution of 45 g. of potassium iodide in 1 l. of saturated sodium acetate solution. The brown tar which separated rapidly solidified, and was crystallised from alcohol in presence of charcoal. The yield of pure 4-iodo-2-nitrotoluene was 85% of the theoretical quantity. The iodo-compound reacted normally with copper bronze. After 20 minutes' heating at  $240^{\circ}$ , the whole was heated at  $260^{\circ}$  for a few minutes, and the cooled product extracted with benzene in presence of charcoal. The benzene was evaporated, and the residue crystallised from alcohol. The dinitroditolyl thus obtained melted at  $175$ – $176^{\circ}$  and its properties agreed with those described by Ullmann and Frentzel (*loc. cit.*).

*Preparation of 3:5'-Dinitrodiphenyl.*—(a) *By the method of Ullmann and Frentzel (loc. cit.).* The exact instructions of these authors were carried out on some dozen occasions. In one or two cases, small quantities of impure dinitrodiphenyl were isolated, but in most of the experiments *m*-chloronitrobenzene was obtained in about 85% of the theoretical yield. (b) *From m-iodonitrobenzene.* The iodo-compound was prepared by the following modification of the usual method (Jacobson, Fertsch, and Heubach, *loc. cit.*). *m*-Nitroaniline (60 g.) was ground with 56 c.c. of concentrated sulphuric acid, 200 c.c. of water were added, and the whole was well ground. The suspension was diazotised at  $5^{\circ}$  with 30.6 g. of sodium nitrite in 150 c.c. of water; addition of the nitrite solution in three

portions, below the surface of the suspension, diminished the formation of the diazoamino-compound. The filtered diazo-solution was poured in small quantities into a well-shaken, boiling solution of 110 g. of potassium iodide and 230 g. of hydrated sodium acetate in 1.5 l. of water. The mixture was then cooled, extracted with carbon tetrachloride, the extract washed with sodium thiosulphate, dried, evaporated, and the residue distilled under diminished pressure. The yield of *m*-iodonitrobenzene (m. p. 38°, b. p. 145—155°/15 mm.) was 70% of the theoretical. When the iodo-compound was heated with copper bronze as described by Ullmann and Bielecki (*loc. cit.*), an average conversion into dinitrodiphenyl of 40% of the theoretical was obtained.

*Reduction of 3:5'-Dinitrodiphenyl.*—The method previously employed by Emde (*loc. cit.*) was found to be unsatisfactory; reduction with iron, water, and ferric chloride also led to small yields of diamine. This readily forms the *disalicylidene* derivative, which separates from benzene in canary-yellow leaflets, m. p. 176—177° (Found: N, 7.3.  $C_{26}H_{20}O_2N_2$  requires N, 7.1%).

*p*-Nitrobenzylidenesalicylidenebenzidine.—The product (m. p. 221—222°, Barzilowski, *loc. cit.*) of interaction of *p*-nitrobenzaldehyde (1 mol.) and benzidine (1 mol.) in hot alcoholic solution was heated under reflux with an alcoholic solution of salicylaldehyde (excess). The red colour of the suspended solid rapidly changed to yellow, and after 30 minutes' boiling the precipitate was collected and crystallised from benzene; yellow prisms, m. p. 210°, were then obtained (Found: N, 10.1.  $C_{26}H_{19}O_3N_3$  requires N, 10.0%).

*p*-Nitrobenzylideneacetylisopropylidenebenzidine.—*p*-Nitrobenzylidenebenzidine was warmed with acetylacetone, and the solution obtained was diluted with alcohol and allowed to cool; brownish-yellow, warty prisms, m. p. 185°, then separated (Found: N, 10.6.  $C_{28}H_{21}O_3N_3$  requires N, 10.9%).

The authors desire to thank the Research Fund Committee of the Chemical Society for a grant in aid of this investigation, and Mr. W. Gordon Adam, of The Gas Light and Coke Company, for a gift of benzene.

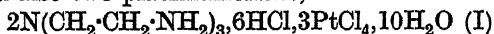
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UNIVERSITY OF LONDON.

[Received, December 30th, 1925.]

## LXII.—*The Complex Salts of $\beta\beta'\beta''$ -Triaminotriethylamine with Nickel and Palladium.*

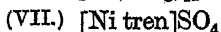
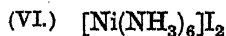
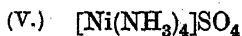
By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

WE have already shown (*Proc. Roy. Soc.*, 1925, **A**, 109, 444) that  $\beta\beta'\beta''$ -triaminotriethylamine may act as a tetra-acidic or a triacidic base, according as the tertiary nitrogen atom exerts or does not exert its basicity. The compound thus gives a tri- and a tetra-hydrochloride, and also two platinichlorides,



and  $2\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_3, 8\text{HCl}, 4\text{PtCl}_4, 20\text{H}_2\text{O}$  (II), two aurichlorides and two rhodichlorides. When, however, the base co-ordinates with metals, it acts solely as a tetramine, and two new types of complex salts were described: thus bivalent platinum of co-ordination number 4 furnishes triaminotriethylamineplatinous iodide,  $[\text{Pt tren}] \text{I}_2$  (III), whilst quadrivalent platinum of co-ordination number 6 gives dichlorotriaminotriethylamineplatonic chloride,  $[\text{Pt tren Cl}_2] \text{Cl}_2$  (IV). In these formulæ, the symbol "tren" denotes one molecule of the base.

The complex compounds which the base furnishes with nickel have now been prepared, and fall into two distinct classes. It is known that bivalent nickel may show a co-ordination number of 4 or 6, furnishing, for example, tetramminonickel sulphate (V) and hexamminonickel iodide (VI).



Triaminotriethylamine similarly gives triaminotriethylaminenickelous sulphate (VII) and tris-triaminotriethylaminebisnickelous tetraiodide (VIII): these two compounds are of the same general type as (V) and (VI) in that the metal shows a co-ordination number of 4 and 6 respectively, although in the latter class three molecules of the tetramine distributed between two atoms of nickel are required if the metal is to show a co-ordination number of 6.

Each of these two classes of complex nickel compounds possesses distinct points of interest. We have pointed out (*loc. cit.*, p. 446) that in compounds of the type of triaminotriethylamineplatinous iodide (III), it might be expected that less strain on the amine molecule would result if two molecules of the base shared two atoms of the metal, thus giving a compound of the type  $[\text{Pt}_2 \text{tren}_2] \text{I}_4$ . The same applies to triaminotriethylaminenickelous sulphate (VII), a compound which by virtue of its high solubility in water lends itself to further investigation. Molecular weight determinations



show, however, that the sulphate has the normal composition denoted by formula (VII), and that one molecule of the base can actually satisfy one atom of the metal; conductivity measurements point to the same conclusion.

With regard to the compound of co-ordination number 6, tris-triaminotriethylaminebisnickelous tetraiodide (VIII), it is difficult to see how this complex, composed of three molecules of the base arranged around the two nickel octahedra, can be other than dissymmetric; all attempts to resolve the tetraiodide, however, proved fruitless, possibly owing to the rapid racemisation of the active complex.

The base has also been co-ordinated with bivalent palladium to give triaminotriethylaminepalladious iodide, a compound precisely similar to the platinous iodide (III).

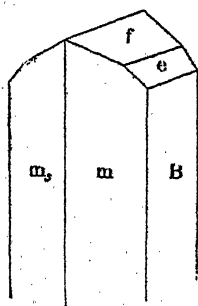
Triaminotriethylamine thus furnishes three distinct types of complex compound, one with bivalent metals of co-ordination number 4, *e.g.*, compounds (III) and (VII), and two with metals of co-ordination number 6, *e.g.*, compounds (IV) and (VIII). These are the first complex compounds to have been prepared with a tetramine; they are, moreover, the first compounds to be described in which an aliphatic tertiary nitrogen atom occupies a co-ordination position.

#### EXPERIMENTAL.

*Preparation of Triaminotriethylaminenickelous Thiocyanate and Tris-triaminotriethylaminebisnickelous Tetraiodide.*—Nickel succinimide,  $[\text{Ni}(\text{N}:\text{C}_2\text{O}_2:\text{C}_2\text{H}_4)_2\cdot 2\text{H}_2\text{O}]\cdot 6\text{H}_2\text{O}$  (Tschugaeff, *Ber.*, 1906, 39, 3197) forms an excellent starting point for the preparation of the co-ordinated derivatives of the metal, since the succinimide residues are easily replaced by aliphatic amines. A mixture of triaminotriethylamine trihydrochloride (32.5 g.) and 33% aqueous caustic soda solution (40.0 c.c.) is therefore warmed on the water-bath until sodium chloride alone remains undissolved. The mixture is poured into a hot solution of nickel succinimide (25.0 g.) in alcohol (750 c.c.). The green solution changes rapidly to blue and is boiled gently for 30 minutes. It is cooled, the precipitated sodium chloride filtered off, and the solution then evaporated gently on the water-bath with the occasional addition of water until it is free from alcohol and of about 60 c.c. in volume. The solution, now of a deep blue, contains a mixture of the two complex ions  $[\text{Ni tren}]^{++}$  and  $[\text{Ni}_2\text{tren}_2]^{++++}$ ; these can be isolated readily as the thiocyanate and tetraiodide, respectively. If the solution is poured into a warm strong solution of potassium thiocyanate, the thiocyanate separates as a pale blue powder or deep blue crystals according to the concentration of the nickel solution; if the original solution is poured into hot strong

potassium iodide, the tetraiodide separates as a reddish-violet powder or deep violet crystals. These two compounds and their derivatives will be described in turn.

*Triaminotriethylaminenickelous thiocyanate*,  $[\text{Ni tren}](\text{SCN})_2$ . The thiocyanate crystallises with great facility from hot aqueous solution in long, very beautiful, deep blue prisms, and two such recrystallisations of the crude product obtained by precipitation with potassium thiocyanate furnish the pure thiocyanate. The latter darkens in colour at  $260^\circ$  and melts with decomposition at  $285^\circ$ ; it is soluble in hot, but almost insoluble in cold water [Found : C, 30.1; H, 5.6; N, 26.3; ionised (SCN), 35.95.  $\text{C}_8\text{H}_{18}\text{N}_6\text{S}_2\text{Ni}$  requires C, 29.9; H, 5.65; N, 26.2; 2(SCN), 36.2%]. Very rarely the thiocyanate



crystallises in long, narrow, and very thin plates: this form is of the same colour as the prismatic variety, and differs from it apparently only in crystalline habit.

Mr. J. W. Notman of Clare College, working under the direction of Mr. A. Hutchinson, F.R.S., has furnished the following report:

"*Triaminotriethylaminenickelous thiocyanate*. System, orthorhombic. Class, bipyramidal.  $a : b : c = 0.736 : 1 : 1.167$ . The substance occurs in fairly well-developed crystals, of elongated prismatic habit, of which four were measured.

Forms present:  $B \{010\}$ ,  $m \{110\}$ ,  $l \{120\}$  observed on one crystal only,  $e \{011\}$ ,  $f \{012\}$ .

Angles	$mm_s$		Meas.	Calc.
	$110 : 1\bar{1}0$	=	$72^\circ 42'$	—
	$Bm$	$010 : 110$	= $53 \ 33$	$53^\circ 39'$
	$Bc$	$010 : 011$	= $40 \ 35$	—
	$ef$	$011 : 012$	= $19 \ 9$	$19 \ 9$
	$ff'$	$012 : 012$	= $60 \ 52$	$60 \ 32$

The crystals were deep blue in colour and, being very opaque, did not lend themselves to optical examination. Some exceedingly thin plates obtained in the case of one preparation enabled straight extinction to be determined."

Both the nickel complexes recorded in this paper are very sensitive to acids, and the addition of hydrochloric acid immediately converts the deep blue of the complex into the pale green of the normal nickel salt. If a warm solution of the thiocyanate is treated with chloroplatinic acid solution, the normal platinichloride (II) of the base is therefore precipitated: if, however, a solution of sodium platinichloride is used, *triaminotriethylaminenickelous platinic tetra-thiocyanate*,  $[\text{Ni tren}]\text{PtCl}_4(\text{SCN})_2$ , is precipitated as a russet-brown powder, insoluble in water: it shrinks at  $211\text{--}213^\circ$ ,

but does not melt below 280° (Found: C, 14.9; H, 2.8; N, 12.8.  $C_8H_{18}N_6Cl_4S_2NiPt$  requires C, 14.6; H, 2.8; N, 12.8%).

*Triaminotriethylaminenickelous Sulphate*,  $[Ni\ tren]SO_4 \cdot 7H_2O$ .—Hot aqueous solutions of the thiocyanate (6.0 g.) and silver sulphate (5.82 g.) were mixed, and the product, after gently boiling for 15 minutes, was filtered and evaporated down to small bulk on the water-bath. The concentrated solution on cooling deposited deep blue crystals; these were recrystallised from a little hot water, filtered, and dried in air. This sulphate, like normal nickel sulphate, gives a series of hydrates. The product obtained as above is the *heptahydrate* (Found:  $SO_4$ , 22.7;  $H_2O$ , 29.4.  $C_8H_{32}O_{11}N_4SNi$  requires  $SO_4$ , 22.5;  $7H_2O$ , 29.5%). The heptahydrate when placed over calcium chloride for 24 hours gives the *dihydrate* as a fine red-dish-blue powder (Found: C, 21.3; H, 6.6;  $SO_4$ , 28.4.  $C_8H_{22}O_6N_4SNi$  requires C, 21.4; H, 6.55;  $SO_4$ , 28.5%). The dihydrate on prolonged exposure to calcium chloride, or when heated in a vacuum at 100°, gives the *anhydrous sulphate* as a pale-blue powder, which does not melt below 300° (Found:  $SO_4$ , 32.25.  $C_8H_{18}O_4N_4SNi$  requires  $SO_4$ , 31.9%).

If the anhydrous sulphate has the formula  $[Ni\ tren]SO_4$ , the molecular weight is 300.9, and the "apparent" molecular weight in dilute aqueous solution (if ionisation is complete) is 150.4. If, however, it has the formula  $[Ni_2tren_2](SO_4)_2$ , the molecular weight is 601.8, and the "apparent" molecular weight 200.6. The results actually obtained by the cryoscopic method are as follows, *c* being the concentration of the anhydrous sulphate expressed as g. in 100 g. of water:

<i>c</i> .....	0.422	1.32	1.70	3.23
"Apparent" mol. wt. ....	160 (157*)	173	180	218

\* Calculated value, correct to only two significant figures.

These results furnish strong evidence that the sulphate has the simple formula  $[Ni\ tren]SO_4$ , and that the "apparent" molecular weight approaches to 150 at great dilution, and increases with increasing concentration as the degree of ionisation falls. If the compound possessed the double formula, it could not show an apparent molecular weight of less than 200. This conclusion is confirmed by the close correspondence between the equivalent conductivities of normal nickelous sulphate and triaminotriethylaminenickelous sulphate at 25°.

Vol. (litres) containing 1 g. equiv. of sulphate .....	128	256	512	1024
Equiv. cond. { $NiSO_4$ .....	88.2	98.9	109.3	117.4
{ $[Ni\ tren]SO_4$ .....	85.9	96.7	106.0	119.2

The values for nickel sulphate are those given by Franke (*Z. physikal. Chem.*, 1895, **16**, 472), those for the tetramine derivative have been determined by Mr. A. F. H. Ward of J  sus College and Mr. L. F. S. Ward of Trinity College, to whom the authors' thanks are due.

*Tristriaminotriethylaminebisnickelous Tetraiodide,*



—The crude reddish-violet iodide obtained by precipitation with potassium iodide in the original preparation is recrystallised three times from hot water, and so obtained in heavy, deep violet crystals : if the hot aqueous solution is too concentrated or is chilled too rapidly, the tetraiodide separates as an oil which subsequently solidifies (Found : C, 18.9; H, 5.4; I, 45.1, 45.1, 45.2; Ni, 10.4, 10.3;  $\text{H}_2\text{O}$ , 5.5.  $\text{C}_{36}\text{H}_{122}\text{O}_7\text{N}_{24}\text{I}_8\text{Ni}_4$  requires C, 19.2; H, 5.5; I, 45.1; Ni, 10.4;  $\text{H}_2\text{O}$ , 5.6%). On one occasion when a small quantity of the iodide was rapidly recrystallised from a little hot water, the *dihydrate* separated (Found : C,\* 19.5, 19.6; H, 5.2, 5.2; N, 15.15; I, 46.2, 46.0.  $\text{C}_{18}\text{H}_{58}\text{O}_2\text{N}_{12}\text{I}_4\text{Ni}_2$  requires C, 19.6; H, 5.3; N, 15.3; I, 46.2%). The anhydrous tetraiodide, obtained by heating either of the above hydrates in a vacuum at  $110^\circ$ , is a pale violet powder, m. p.  $307\text{--}309^\circ$  (decomp.) (Found : I, 47.4.  $\text{C}_{18}\text{H}_{54}\text{N}_{12}\text{I}_4\text{Ni}_2$  requires I, 47.6%).

If, after the crude tetraiodide has been precipitated in the original preparation, the filtrate is treated with saturated potassium thiocyanate solution, triaminotriethylaminebisnickelous thiocyanate separates in fair yield and after two recrystallisations is pure; both complexes can thus be isolated from the same preparation.

The *tetrabromide*,  $[\text{Ni}_2\text{tren}_3]\text{Br}_4$ , can be obtained in small yield by treating the final solution in the original preparation with strong sodium bromide solution, or in better yield by treating a saturated solution of the tetracamphorsulphonate described later with sodium bromide. It is obtained on recrystallisation as a pale reddish-blue, anhydrous powder, which does not melt below  $290^\circ$  (Found : H, 6.1; Br, 36.4, 36.7; Ni, 13.6.  $\text{C}_{18}\text{H}_{54}\text{N}_{12}\text{Br}_4\text{Ni}_2$  requires H, 6.2; Br, 36.5; Ni, 13.4%).

*Attempted Resolution of the Tristriaminotriethylaminebisnickelous Complex,  $[\text{Ni}_2\text{tren}_3]^{++++}$ .*—The *tetra-d-  -bromocamphor-  -sulphonate*,  $[\text{Ni}_2\text{tren}_3](\text{C}_{10}\text{H}_{14}\text{O}_4\text{BrS})_4$ . Solutions of 16.0 g. of the tetraiodide ( $3\frac{1}{2}\text{H}_2\text{O}$ ) and 23.56 g. of silver *d-  -bromocamphor-  -sulphonate*, each in 75 c.c. of hot water, were mixed and the product, after gentle

\* Throughout this paper, repeated analytical results refer to analyses of different preparations of the compound, and not merely to repeated analyses of the same preparation : the figures given for this dihydrate are the only exception.

boiling, was filtered and evaporated until crystals appeared on the surface. The solution was now cooled and filtered, and the crystalline residue three times recrystallised from water. The anhydrous *tetra-d-bromocamphorsulphonate* was thus obtained as a pale violet, crystalline powder, which shrinks at  $180^\circ$  and melts with decomposition at  $183\text{--}185^\circ$  (Found: H, \* 6.2; Br, 17.8; S, 7.05; Ni, 6.5.  $\text{C}_{58}\text{H}_{110}\text{O}_{16}\text{N}_{12}\text{Br}_4\text{S}_4\text{Ni}_2$  requires H, 6.2; Br, 17.8; S, 7.1; Ni, 6.5%).

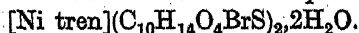
The tetrabromocamphorsulphonate is so slightly soluble in water that it could not be reconverted by double decomposition into the bromide or iodide. The hot aqueous solution was therefore added carefully to a hot dilute solution of sodium picrate, and the *tetrapicrate*,  $[\text{Ni}_2\text{tren}_3](\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_4 \cdot 3\text{H}_2\text{O}$ , precipitated as a fine, dark yellow powder, which when filtered, washed with water and alcohol, and air-dried melted with decomposition at  $205\text{--}206^\circ$  (Found: C, 33.25; H, 4.5; N, 22.2.  $\text{C}_{42}\text{H}_{68}\text{O}_{31}\text{N}_{24}\text{Ni}_2$  requires C, 33.1; H, 4.5; N, 22.1%).

This tetrapicrate was found to be identical in composition and melting point with that obtained directly from the tetraiodide; it is only very slightly soluble in boiling water and insoluble in all ordinary organic solvents except formamide. No rotation could be detected in a 0.5% solution of the picrate in formamide in a 2-dcm. tube: stronger solutions could not be used owing to the high absorption of light.

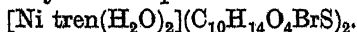
The *tetra-d-camphor- $\beta$ -sulphonate*,  $[\text{Ni}_2\text{tren}_3](\text{C}_{10}\text{H}_{15}\text{O}_4\text{S})_4$ . Solutions of the tetraiodide (19.0 g.) and silver *d*-camphor- $\beta$ -sulphonate (22.8 g.), each in warm water (80 c.c.), were mixed, and the product after gentle boiling was filtered and then evaporated until crystals appeared in the solution. The latter was cooled and filtered, and the crystallised product three times recrystallised from warm water. The *tetra-d-camphorsulphonate* was thus obtained as a reddish-violet, crystalline powder, which shrinks at  $230^\circ$  and melts at  $233\text{--}235^\circ$ : it is appreciably more soluble in water than the corresponding bromocamphorsulphonate (Found: H, 7.8; S, 8.9; Ni, 7.95.  $\text{C}_{58}\text{H}_{114}\text{O}_{16}\text{N}_{12}\text{S}_4\text{Ni}_2$  requires H, 7.8; S, 8.7; Ni, 7.9%). A warm solution of the camphorsulphonate was mixed with that of potassium iodide, and the crystals which separated on cooling were rapidly recrystallised from a little hot water, the pure tetraiodide being thus obtained (Found: I, 45.1%). A 2% aqueous solution of this tetraiodide in a 4-dcm. tube gave no perceptible rotation.

Attempts to prepare a crystalline tartrate of the complex failed, only syrupy solutions being obtained.

\* All the camphor derivatives (and certain others) recorded in this paper gave low and irregular values for carbon, but satisfactory values for hydrogen.

*Triaminotriethylaminenickelous d-bromocamphorsulphonate,*

Attempts were also made to prepare the above tetra-*d*-bromocamphor- $\pi$ -sulphonate by double decomposition of the tetraiodide with ammonium *d*-bromocamphorsulphonate. It was found, however, that when solutions of the tetraiodide (4 g.) and an excess of the ammonium sulphonate (6 g.), each in warm water (20 c.c.), were mixed, and the product warmed on the water-bath, ammonia was evolved, and crystals soon appeared on the surface. This product was twice recrystallised from warm water, and finally obtained as beautiful, bluish-violet, crystalline plates. These on analysis proved to be *triaminotriethylaminenickelous d-bromocamphorsulphonate* (Found: Br, 18.6; S, 7.5; Ni, 6.65;  $\text{H}_2\text{O}$ , 4.2.  $\text{C}_{26}\text{H}_{50}\text{O}_{10}\text{N}_4\text{Br}_2\text{S}_2\text{Ni}$  requires Br, 18.55; S, 7.4; Ni, 6.8;  $2\text{H}_2\text{O}$ , 4.2%). Heating in a vacuum at  $110^\circ$  gives the pale blue, anhydrous product, m. p.  $263\text{--}266^\circ$  (decomp.). The identity of this compound was further confirmed by treating its warm aqueous solution with potassium thiocyanate solution, when triaminotriethylaminenickelous thiocyanate separated, and when once recrystallised was pure (Found: N, 25.85%). This degradation of the nickel complex of co-ordination number 6 to that of co-ordination number 4 by the action of an ammonium salt was found to be general, and to follow presumably the equation  $[\text{Ni}_2\text{tren}_3]\text{X}_4 + 4\text{NH}_4\text{X}' = 2[\text{Ni tren}]\text{X}_2 + \text{tren } 4\text{HX}' + 4\text{NH}_3$ . It is noteworthy that the third molecule of the tetramine in the higher complex is evicted but not replaced by the ammonia under these conditions, and all attempts made to prepare compounds having the complex  $[\text{Ni tren}(\text{NH}_3)_2]^{++}$  failed. In the particular case of the *d*-bromocamphorsulphonate described above, the colours of the dihydrate (bluish-violet) and the anhydrous product (pale blue) are characteristic of nickel complexes having co-ordination numbers of 6 and 4 respectively, and therefore the dihydrate has probably the composition



*Triaminotriethylaminepalladious Iodide*,  $[\text{Pd tren}]\text{I}_2$ .—A warm solution of triaminotriethylamine trihydrochloride (5.4 g.) in 33% aqueous caustic soda solution (7.4 c.c.) is added to a solution of palladium dichloride (3.0 g.) in hot water (70 c.c.). An amorphous, yellow precipitate at once appears, but redissolves when the solution is heated on the water-bath. After heating for 2 hours, the solution is evaporated to small bulk, filtered, and mixed with warm strong potassium iodide solution. The cream-coloured precipitate is filtered off, and recrystallised from much hot water, in which the iodide is only moderately soluble. The *triaminotriethylaminenickelous iodide* is thus obtained as a fine, cream-coloured powder,

which after drying over sulphuric acid darkens in colour at  $220^{\circ}$  and melts at  $224-226^{\circ}$  (decomp.) (Found: C, 14.1; H, 3.9; I, 49.6; Pd, 20.9.  $C_6H_{18}N_4I_2Pd$  requires C, 14.2; H, 3.6; I, 50.1; Pd, 21.1%).

If instead of adding potassium iodide to the above solution, the latter is chilled, made just acid with hydrochloric acid, and treated with an excess of dilute palladium dichloride solution, a fine dark brown precipitate separates. The latter redissolves if the solution is warmed, and on filtering and cooling, long, chocolate-coloured needles separate. These crystals decompose largely if an attempt is made to recrystallise them from boiling water, and their identity is therefore uncertain; they would appear to be *triaminotriethylamine-palladious palladiochloride*,  $[Pd\ tren]PdCl_6 \cdot H_2O$ , and owe their formation presumably to partial atmospheric oxidation of the palladious chloride solution (Found: C, 12.3; H, 3.8; Cl, 35.3; Pd, 35.7.  $C_6H_{20}ON_4Cl_6Pd_2$  requires C, 12.2; H, 3.4; Cl, 36.0; Pd, 36.15%).

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### LXIII.— $\gamma\gamma'\gamma''$ -Triaminotripropylamine and its Complex Compounds with Nickel.

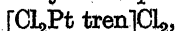
By FREDERICK GEORGE MANN and WILLIAM JACKSON POPE.

THE preparation of  $\gamma\gamma'\gamma''$ -triaminotripropylamine is similar to that of  $\beta\beta'\beta''$ -triaminotriethylamine, for molten phthal- $\gamma$ -bromopropylimide on treatment with gaseous ammonia gives  $\gamma\gamma'\gamma''$ -triphthalimidotripropylamine hydrobromide, which on hydrolysis furnishes the required base. Whereas, however, the tertiary nitrogen atom in triaminotriethylamine is so feebly basic that the amine may act as a tri- or a tetra-acidic base, that in triaminotripropylamine, by virtue of its greater distance from the primary amine groups, is strongly basic, and the amine therefore always acts as a tetra-acidic base. The strongly basic character of the tertiary amine group in triaminotripropylamine causes the synthesis to follow a rather different course from that of the corresponding ethyl base. Ammonia reacts with phthal- $\beta$ -bromoethylimide to give triphthalimidotriethylamine, mixed with about 12% of the hydrobromide of this base: phthal- $\gamma$ -bromopropylimide, however, gives solely triphthalimidotripropylamine hydrobromide, and none of the free base. The hydrobromide, moreover, is largely contaminated with various amorphous by-products, and the yield of the triphthalimido-compound is therefore low.

It has been shown (preceding paper) that nickel succinimide on treatment with triaminotriethylamine gives a mixture of two com-

plex ions, the bivalent triaminotriethylaminenickelous ion,  $[\text{Ni tren}]^{++}$ , in which the metal shows a co-ordination number of 4, and the quadrivalent tristriaminotriethylaminebisnickelous ion,  $[\text{Ni}_2 \text{tren}_3]^{++++}$ , in which the metal has a co-ordination number of 6. Nickel succinimide on treatment with triaminotripropylamine gives, however, one complex of the first type only, and the triaminotripropylamine-nickelous ion,  $[\text{Ni trpn}]^{++}$ , in which the metal shows a co-ordination number of 4, can be precipitated as the thiocyanate. The symbol "trpn" is here used to denote one molecule of the tetramine. This complex ion is less stable and less strongly electropositive than the corresponding ethyl complex ion; the thiocyanate undergoes slight decomposition even on recrystallisation from hot water, whilst precipitation with potassium iodide in the original preparation furnishes the hydroxy-iodide of the above complex. The normal iodide is prepared by the double decomposition of some far more stable salt such as the nitrate.

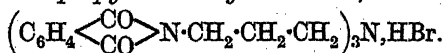
No complex compound of triaminotripropylamine with nickel or with platinum in which the metal showed a co-ordination number of 6 could be isolated. It would seem, therefore, that the very well defined dichlorotriaminotriethylamineplatinic chloride,



has no stable propyl homologue.

#### EXPERIMENTAL.

##### *Triphthalimidotripropylamine Hydrobromide,*



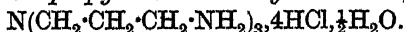
—A stream of dry ammonia gas is passed through molten phthal- $\gamma$ -bromopropylimide at  $150^\circ$  until the product becomes too viscous to allow further passage of the gas, the reaction being about twice as rapid as that with phthal- $\beta$ -bromoethylimide under like conditions. The cold pale-yellow product (with containing tube) is pulverised, and twice extracted with boiling alcohol: the residue is washed with water, and then recrystallised from hot acetic acid. The solution, when filtered and cooled, deposits  $\gamma\gamma'\gamma''$ -triphthalimidotripropylamine hydrobromide with one molecule of acetic acid of crystallisation. This product, when washed with acetic acid and ether and dried in the air, is pure; on heating, it liberates acetic acid at  $100$ – $105^\circ$ , and finally melts at  $243$ – $244^\circ$ , i.e., at the melting point of the hydrobromide itself (Found: C, 58.5; H, 5.0; Br, 11.4.  $\text{C}_{35}\text{H}_{35}\text{O}_8\text{N}_4\text{Br}$  requires C, 58.4; H, 4.9; Br, 11.1%). The hydrobromide itself can be obtained by heating the above product in a vacuum at  $100^\circ$ , or by crystallisation from a large volume of very dilute hydrobromic acid, from which the



hydrobromide separates in colourless needles, m. p. 243—245° (Found : Br, 12.1.  $C_{33}H_{31}O_6N_4Br$  requires Br, 12.1%).

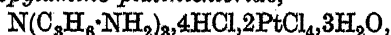
*Triphthalimidotripropylamine*,  $(C_6H_4 \cdot C_2O_2 \cdot N \cdot C_3H_7)_3N$ .—The hydrobromide with acetic acid of crystallisation (2 g.) is dissolved in boiling water (450 c.c.), and to the clear solution is added a slight excess of *N*-sodium hydroxide (6.0 c.c.). A white precipitate of *triphthalimidotripropylamine* immediately separates, and when filtered, washed with boiling water, and twice recrystallised from alcohol, is obtained in fine needles, m. p. 150—151° (Found : C, 68.8; H, 5.2.  $C_{33}H_{30}O_6N_4$  requires C, 68.5; H, 5.2%).

*γ'γ''-Triaminotripropylamine Tetrahydrochloride*,



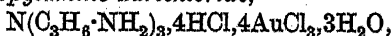
—Triphthalimidotripropylamine hydrobromide with acetic acid of crystallisation (10 g.) and hydrochloric acid (300 c.c., 1:1 by volume) are boiled under reflux. The solution becomes clear in about 4 hours, and after 7 hours is chilled, the phthalic acid separated, and the filtrate evaporated to small bulk. The tetrahydrochloride is so soluble in water that it cannot be crystallised, and prolonged evaporation of its solution merely gives a syrup: the concentrated solution is therefore poured into alcohol, and the heavy syrup which separates, solidifies on standing and stirring to a crystalline mass of the tetrahydrochloride, which is filtered off and washed with alcohol. The *tetrahydrochloride* is thus obtained as slightly deliquescent, white crystals which melt with foaming at 227—229°; the water of crystallisation is not liberated on heating in a vacuum at 100° (Found : C, 31.1; H, 8.2; Cl, 41.3, 41.7.  $C_{18}H_{58}ON_8Cl_8$  requires C, 31.5; H, 8.45; Cl, 41.3%).

*Triaminotripropylamine platinichloride*,



is prepared in the usual way, and when recrystallised from a little water separates in orange-coloured needles (Found : C, 10.3; H, 3.2; Pt, 36.7;  $H_2O$ , 4.9.  $C_9H_{34}O_3N_4Cl_{12}Pt_2$  requires C, 10.2; H, 3.2; Pt, 36.8;  $3H_2O$ , 5.1%). The anhydrous material darkens at 250° and melts with decomposition at 257—258°.

*Triaminotripropylamine aurichloride*,



separates when concentrated solutions of the tetrahydrochloride and of potassium aurichloride are mixed. It is filtered, washed with water, and dried without recrystallisation; the orange-yellow needles, m. p. 191—192° (decomp.), are even more soluble in alcohol and acetone than in water (Found : C, 6.9; H, 2.0; Au, 49.4, 49.5.  $C_9H_{34}O_3N_4Cl_{12}Au_4$  requires C, 6.75; H, 2.1; Au, 49.2%).

*Triaminotripropylamine picrate*,  $N(C_3H_7 \cdot NH_2)_3, 4C_6H_4O_7N_3 \cdot H_2O$ , is almost insoluble in the usual liquids, but can be recrystallised

from boiling water, one litre of which dissolves about 1 g. of the picrate. The latter separates in pale yellow needles which soften at 190° and melt with decomposition at 222° (Found: C, 35.2; H, 3.5.  $C_{33}H_{38}O_{26}N_{16}$  requires C, 35.3; H, 3.4%).

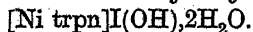
*Tribenzoyltriaminotripropylamine*,  $N(C_6H_5NHCO\cdot C_6H_5)_3$ , prepared in the usual way, is obtained after three recrystallisations from anhydrous acetone as fine, white crystals, m. p. 129—131° (Found: C, 72.1; H, 7.2.  $C_{30}H_{36}O_3N_4$  requires C, 71.9; H, 7.25%).

*The Co-ordination Derivatives of Triaminotripropylamine.*

*Triaminotripropylaminenickelous thiocyanate*,  $[Ni\ trpn](SCN)_2$ .—The tetrahydrochloride of the base (12.0 g.) is warmed with 33% aqueous caustic soda solution (16.0 c.c.) until sodium chloride alone remains undissolved: the mixture is then added to a hot solution of nickel succinimide (8.5 g.) in alcohol (250 c.c.). The colour of the solution changes rapidly from pale green to blue. The solution is now treated precisely as in the preparation of the corresponding ethyl derivative (p. 483), and the concentrated aqueous solution is filtered directly into a cold strong solution of potassium thiocyanate. The fine precipitate is filtered off and twice recrystallised from hot water, from which the *triaminotripropylaminenickelous thiocyanate* separates on rapid cooling in pale lilac-blue, crystalline leaflets, and on slow cooling in long needles of the same colour. The difference between these two forms, as in the case of the corresponding ethyl derivative, is apparently solely one of crystalline habit (Found: C, 36.6; H, 6.55; Ni, 16.2.  $C_{11}H_{24}N_6S_2Ni$  requires C, 36.4; H, 6.7; Ni, 16.2%). The thiocyanate melts at 260—261° with decomposition; it is far less stable than the corresponding ethyl compound, and when recrystallised from hot water always leaves behind on the filter a small quantity of an amorphous green product, presumably nickel hydroxide.

*Triaminotripropylaminenickelous Iodide*,  $[Ni\ trpn]I_2\cdot 1\frac{1}{2}H_2O$ .—The thiocyanate in hot aqueous solution is treated with a solution of the calculated quantity of silver nitrate, and the product, after filtering, evaporated to small bulk. The cold concentrated solution is added to a cold saturated potassium iodide solution, and the crystalline precipitate filtered off and washed with a little water, alcohol, and ether. The *iodide* is thus obtained as a fine, apple-green, crystalline powder (Found: I, 48.05; Ni, 11.0.  $C_{13}H_{54}O_3N_8I_4Ni_2$  requires I, 48.1; Ni, 11.1%).

*Triaminotripropylaminenickelous Hydroxyiodide*,



—If the warm concentrated aqueous solution obtained by treating nickel succinimide with the amine is mixed with about twice its

volume of hot strong potassium iodide solution, fine, sea-green, crystalline leaflets rapidly appear. These crystals consist of the above *hydroxyiodide* combined with potassium iodide, and have the composition  $2[\text{Ni trpn}]\text{I}(\text{OH})\cdot\text{KI}\cdot 2\text{H}_2\text{O}$ . This compound is decomposed, however, even by cold water, and the preparation of the pure material is therefore almost impossible: slight dissociation occurs when the crystals are washed even with a little alcohol to free them from mother-liquor, and various preparations always give in consequence a low iodine and high carbon value (Found: C, 22.7; H, 5.3; N, 11.0; I, 37.7; Ni, 11.5.  $\text{C}_{18}\text{H}_{54}\text{O}_4\text{N}_8\text{I}_3\text{NiK}$  requires C, 22.0; H, 5.5; N, 11.4; I, 38.7; Ni, 11.9%).

If the mother-liquor after the separation of these crystals is treated further with potassium thiocyanate solution, a small precipitate of triaminotripropylaminenickelous thiocyanate is obtained.

When the green crystals of the potassium iodide addition product are dissolved in warm water, a deep blue solution is at once obtained, and, on cooling, deep blue crystals of *triaminotripropylaminenickelous hydroxyiodide*,  $[\text{Ni trpn}]\text{I}(\text{OH})\cdot 2\text{H}_2\text{O}$ , separate. The hydroxyiodide is quite stable in the presence of water, and can be recrystallised repeatedly from boiling water without apparent change (Found: C, 25.5; H, 6.3; N, 13.0; I, 29.5; Ni, 13.5.  $\text{C}_9\text{H}_{25}\text{O}_3\text{N}_4\text{INi}$  requires C, 25.3; H, 6.85; N, 13.1; I, 29.7; Ni, 13.75%). This compound when heated in a vacuum at  $100^\circ$  readily loses its water of crystallisation, but at the same time undergoes slight further hydrolysis, and the anhydrous product is therefore never quite pure. When the hydroxyiodide in strong aqueous solution is treated with strong potassium iodide solution, the sea-green crystals of the above potassium iodide addition product once again separate, and when recrystallised from water again furnish the pure deep blue hydroxyiodide. Moreover, when the hydroxyiodide in aqueous solution is treated with potassium thiocyanate solution, a rapid precipitation of triaminotripropylaminenickelous thiocyanate occurs, and the latter when once recrystallised from hot water is pure (Found: N, 23.2.  $\text{C}_{11}\text{H}_{24}\text{N}_6\text{S}_2\text{Ni}$  requires N, 23.2%). Aqueous solutions of the hydroxyiodide are distinctly alkaline, and on exposure to air absorb carbon dioxide.

In view of the ready formation and great stability of dichlorotriaminotriethylamineplatinic chloride,  $[\text{Cl}_2\text{Pt tren}]\text{Cl}_2$  (p. 482) many experiments were made to prepare the corresponding propyl derivative. No definite evidence of the formation of such a compound could be obtained, however, and the attempt was finally abandoned.

# LXIV.—The Resolution of *dl*-Alanine and the Formation of *trans*-2:5-Dimethylpiperazine.

By FREDERIC BARRY KIPPING and WILLIAM JACKSON POPE.

THE  $\alpha$ -2:5-dimethylpiperazine of Stoehr (*J. pr. Chem.*, 1893, 47, 494; 1897, 55, 49) was identified by Pope and Read (*J.*, 1912, 101, 2327; 1914, 105, 219) as the *trans*-isomeride; the same compound was obtained by Hoyer (*Z. physiol. Chem.*, 1902, 34, 347) by the reduction of lactimide,  $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CHMe} \\ \text{CHMe} \cdot \text{CO} \end{smallmatrix} \text{NH}$ . The latter compound would therefore appear to be internally compensated or *trans*-3:6-diketo-2:5-dimethylpiperazine produced by anhydride formation from a molecule each of *d*- and *l*-alanine; this conclusion, as will be shown later, is not necessarily correct. The two optically active alanines, on the other hand, yield optically active anhydrides (E. Fischer, *Ber.*, 1906, 39, 453) which are necessarily the *d*- and *l*-*cis*-3:6-diketo-2:5-dimethylpiperazines. It might be expected that on reduction the latter substances would yield the *d*- and *l*-*cis*-2:5-dimethylpiperazines; the racemic compound of these two isomerides should be represented by the  $\beta$ -2:5-dimethylpiperazine of Stoehr (*loc. cit.*), but Pope and Read were unable to separate such a compound from the material which they examined.

It thus seemed desirable to reduce the anhydride of one of the optically active alanine anhydrides or *cis*-3:6-diketo-2:5-dimethylpiperazines for the purpose of isolating and further characterising the *d*- and *l*-*cis*-2:5-dimethylpiperazines which were presumably associated in Stoehr's  $\beta$ -compound. A certain quantity of *d*-alanine was prepared by the hydrolysis of silk as described by Fischer (*Ber.*, 1906, 39, 462), but the process, although satisfactory, is tedious. The preparation was hastened by preparing *dl*-alanine from acetaldehyde, potassium cyanide and ammonium chloride by the method of Zelinsky and Stadnikov (*Ber.*, 1908, 41, 2061) and resolving this into its optically active components.

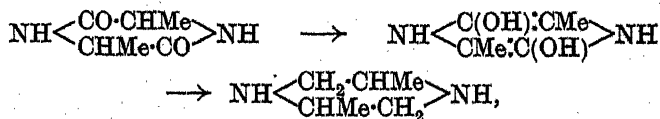
Fischer (*Ber.*, 1899, 32, 2459) resolved benzoyl-*dl*-alanine by crystallisation with cinchonine, and Gibson and Pope (*J.*, 1912, 101, 939) improved this method by the alternate use of strychnine and brucine; the hydrolysis to *d*- and *l*-alanine proceeds, however, only with difficulty. Gibson and Simonsen (*J.*, 1915, 107, 798) resolved *dl*-*p*-toluenesulphonylalanine by crystallisation with strychnine and brucine, and Colombano and Sanna (*Atti R. Accad. Lincei*, 1913, 22, 292) resolved *dl*-alanine by crystallising its ethyl ester with bromocamphorsulphonic acid.

None of these methods proved satisfactory for preparing the

optically active alanines in quantity and we therefore devised a new one. It was found that *d*-hydroxymethylenecamphor and *d*-chloromethylenecamphor do not condense with *dl*-alanine, but that condensation occurs readily with the ethyl ester of alanine; the method of resolution by means of *d*-hydroxymethylenecamphor described by Pope and Read (J., 1914, 105, 219) is therefore applicable and the condensation products can be hydrolysed by concentrated hydrochloric acid, yielding the optically active alanines. This method of resolving *dl*-alanine seems to be the most convenient yet described; by its aid *l*-alanine has been separated in quantity from the racemic compound.

Several methods for converting the *d*- and *l*-alanines into the *d*- and *l*-*cis*-3 : 6-diketo-2 : 5-dimethylpyperazines, or the optically active lactimides, were studied. Hoyer's method of heating alanine in dry hydrogen chloride at 180–200°, boiling the product with lead hydroxide, and removing the metal by hydrogen sulphide gave poor yields. One method described by Fischer (*Ber.*, 1906, 39, 467), in which the ethyl ester of alanylalanine, prepared from alanine ethyl ester and alanyl chloride, is treated with gaseous ammonia, also gives poor yields. Fischer's second method (*Ber.*, 1906, 39, 543), in which the ethyl ester of alanine is preserved for several weeks, is satisfactory and gives a yield of about 70%.

When the optically active lactimides, which have necessarily the *cis*-configuration, were reduced with sodium and alcohol, the chief product, and indeed the only one which could be isolated, was the potentially optically inactive *trans*-2 : 5-dimethylpyperazine identified by Pope and Read. It thus seems clear that the lactimide undergoes enolisation during reduction in accordance with the scheme



and that the original *cis*-compound thus becomes converted into the *trans*-2 : 5-dimethylpyperazine accompanied by little, if any, of the *cis*-isomeride. No evidence is thus obtainable as to whether inactive lactimide is the racemic or *cis*-compound or the internally compensated or *trans*-compound.

#### EXPERIMENTAL.

*dl*-Alanine, prepared by Zelinsky and Stadinov's method, was converted into its ethyl ester, which was then heated for 2 hours on the water-bath with an equimolecular quantity of *d*-hydroxymethylenecamphor. On pouring into water, extracting with light

petroleum, and evaporating the petroleum solution after drying with potassium carbonate, an oil was obtained which readily crystallised; the crystalline product was repeatedly crystallised from light petroleum until its melting point became constant at 108–109°. The substance thus obtained in long, white needles is the *d*-methylene-camphor-*l*-alanine ethyl ester,  $C_8H_{14} \begin{smallmatrix} \diagup C:CH-NH \cdot CHMe \cdot CO_2Et \\ \diagdown CO \end{smallmatrix}$

(Found: C, 68.9; H, 8.9.  $C_{16}H_{25}O_3N$  requires C, 68.8; H, 9.0%). The substance is so soluble in most organic solvents that it can only be conveniently crystallised from light petroleum. 0.1008 Gram, made up to 20 c.c. with absolute alcohol, gave  $\alpha_{Hg \text{ green}} = +2.58^\circ$  in a 2-dcm. tube at 20°; whence  $[\alpha]_{Hg \text{ green}} = +256^\circ$ .

This compound, when treated by the bromine method of Pope and Read, yielded only resinous products from which alanine could not be separated; it is, however, hydrolysed by distillation in steam after admixture with concentrated hydrochloric acid. Hydroxy-methylenecamphor distils away and *l*-alanine hydrochloride remains behind; the hydrochloric acid is removed with the aid of lead hydroxide, the excess of the latter by hydrogen sulphide, and the *l*-alanine then separated by crystallisation from the residual aqueous solution. 1.8761 Gram, made up to 20 c.c. with 1.25*N*-hydrochloric acid solution, gave  $\alpha_{Hg \text{ green}} = -3.22^\circ$  in a 2-dcm. tube at 20°; whence  $[\alpha]_{Hg \text{ green}} = -12.2^\circ$ ; this value is numerically identical with that given by *d*-alanine prepared from silk, but is, of course, of opposite sign. This simple type of method will be further studied in its applications to the resolution of racemic aminocarboxylic acids.

*Reduction of l-Lactimide.*—*l*-Alanine was converted into its ethyl ester and preserved for several weeks until solidification had apparently become complete; after crystallisation from alcohol a 70% yield of *l*-lactimide was obtained. The product melted at 272° and showed  $[\alpha]_D^{20} = +29.1^\circ$  in a 2% alcoholic solution. The *l*-lactimide (6 g.) was treated with absolute alcohol (300 c.c.), and sodium (32 g.) gradually added with constant shaking. After removal of the alcohol, the reduction product was benzoylated; the only separable product was the optically inactive dibenzoyl-*trans*-2:5-dimethylpiperazine (0.8 g.) of Pope and Read. The identity of the product was confirmed by mixed melting-point determinations with a sample of the latter substance; each, and the mixtures, melted at 227–228°.

No better yields were obtained by reducing the *l*-lactimide in amyl-alcoholic solution and it is noteworthy that Gaurilov (*Bull. Soc. chim.*, 1925, 37, 1651) obtained only a 15% yield of piperazine by this mode of reducing 2:5-diketopiperazine. The lactimide

could not be reduced by colloidal palladium or platinum, by calcium or calcium hydride and alcohol, or by aluminium amalgam in aqueous-alcoholic solution.

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CAMBRIDGE.

[Received, January 18th, 1926.]

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## NOTES.

*Air Oxidation of Titanous Sulphate Solution. Vanadous Sulphate, a New and Powerful Reducing Agent.* By A. S. RUSSELL.

THE powerful reducing agent, titanous sulphate, is used less than it might be on account of the trouble of preserving it from oxidation by air. I am not aware than any worker with this reagent has said that this is unnecessary. Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," 2nd ed., 1925, p. 62), who have the largest experience of this reagent, say that any results obtained without taking the precaution of preventing air oxidation are valueless. My experience is different. When a solution of titanous sulphate in 4*N*-sulphuric acid is prepared from titanous sulphate by Nakazono's rapid method (*J. Chem. Soc. Japan*, 1921, 42, 526), and kept in a burette exposed to air, I find that its titre when standardised with *N*/10-permanganate remains constant for 12 hours. It follows that precautions to exclude air are unnecessary. It is also a consequence that if titanium itself be determined by reducing titanous sulphate with zinc amalgam and titrating the liquid after separation with permanganate, the work can be carried out in air if the acidity of the titanium solution is 4*N*-sulphuric acid. I confirmed this by alternately reducing with zinc amalgam and oxidising with *N*/10-permanganate four times a volume of titanous sulphate of known concentration without excluding air. The titres were constant and equal to that calculated on the assumption that the reduction was quantitative. Titanous sulphate thus resembles ferrous and uranous sulphates in being stable in air at the ordinary temperature if in 4*N*-sulphuric acid.

It is not necessary to adopt the excellent but elaborate method of Knecht and Hibbert (*op. cit.*, p. 63) for preserving titanous sulphate solution for a long time. It is simpler to have a solution of titanous sulphate in 4*N*-sulphuric acid and, whenever titanous sulphate is needed, to reduce the volume required with zinc amalgam for 1 minute, decant the liquid into a flask, transfer to a burette, and

immediately before use standardise it against  $N/10$ -permanganate. I find it is not oxidised by the air when run into hot or boiling solutions reduced by it. I find also that titanous sulphate is not less powerful as a reducing agent than the chloride and that the reducing power is unaffected by the presence of the free sulphuric acid. The sulphate solution is consequently simpler to use than the chloride, because in practice back titrations are done with permanganate as well as with ferric alum.

Vanadous sulphate has not, I think, been previously used as a reducing agent. I find that it is a more powerful reducing agent than titanous sulphate, reducing with greater ease all the inorganic and organic substances reduced by the latter. It reduces titanous sulphate itself in the cold. It lies between cadmium and tin in its reducing power in  $2N$ -sulphuric acid, whereas titanous sulphate was found to lie between lead and copper. It is, as is to be expected, much more susceptible to air oxidation, but not to such an extent that precautions to exclude air when using it are essential. A  $N/10$ -solution in  $10N$ -sulphuric acid is not measurably oxidised by air when kept for an hour in a burette. It may therefore be used without excluding air in volumetric work which can be completed within that time. It is prepared by the same method and as quickly as titanous sulphate.—DR. LEE'S LABORATORY, CHRIST CHURCH, OXFORD. [Received, November 3rd, 1925.]

*The Effect of Heat on Chloral Hydrate.* By JAMES DENIS  
MOUNFIELD and JOHN KERFOOT WOOD.

THE temperature at which the dissociation of chloral hydrate commences is unknown. It is complete at  $78^{\circ}$ , and the variability of the melting point suggests that it may occur to a considerable extent at about  $50^{\circ}$ . Pope (J., 1899, 75, 455) has suggested that two modifications of chloral hydrate may exist, but the work of Van Rossem and Jaeger (*Z. physikal. Chem.*, 1908, 62, 701) would appear to discredit this view.

To obtain further information on these matters, the authors have conducted dilatometric and tensimetric measurements with chloral hydrate. Repeated experiments with "liquid paraffin B.P." as the indicating liquid showed that chloral hydrate suffers a change of volume at  $32^{\circ}$ ; similar indications were given by samples which had been maintained at  $20^{\circ}$  and  $40^{\circ}$  for several days and which were slowly heated and cooled, respectively.

In the tensimeter experiments, the vapour pressure was measured at small intervals of temperature between  $15^{\circ}$  and  $40^{\circ}$ . The results are in Tables I and II, the former referring to rising and the



latter to falling temperature; the pressures indicate millimetres of  $\alpha$ -bromonaphthalene.

TABLE I.

Temp.	Press.	Temp.	Press.
15.65°	6.12	31.10°	17.29
18.90	8.16	31.90	18.08
19.80	8.67	33.00	19.33
21.30	9.53	34.00	20.31
23.01	10.69	34.55	21.20
24.80	11.96	35.50	22.38
26.70	13.40	36.50	23.95
27.10	13.78	37.30	24.82
28.50	14.99	37.73	25.34
29.50	15.90	38.05	26.20
30.35	16.63	38.50	26.90

TABLE II.

Temp.	Press.	Temp.	Press.
17.29	37.70°	25.29	30.00°
37.25	24.60	28.70	15.22
36.43	23.61	27.60	14.08
35.90	22.72	25.70	12.59
34.95	21.70	24.00	11.20
33.60	19.80	21.80	10.00
32.50	18.60	20.85	9.21
31.50	17.81	19.45	8.42
31.20	17.56	—	—

The values obtained in the two series of experiments are in agreement and show the complete absence of a break in the vapour pressure curve in the vicinity of 32°; Ramsay and Young (*Phil. Trans.*, 1886, **177**, 76), from observations made at much larger intervals of temperature, also obtained a smooth curve. From the absence of a break in the vapour pressure curve it would appear most probable that the change which occurs at 32° does not correspond to a change of modification, but marks the commencement of the dissociation of chloral hydrate.—MUNICIPAL COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [Received, October 10th, 1925.]

*Preparation of Ethylene Bromohydrin.* By FREDERICK HENRY McDOWALL.

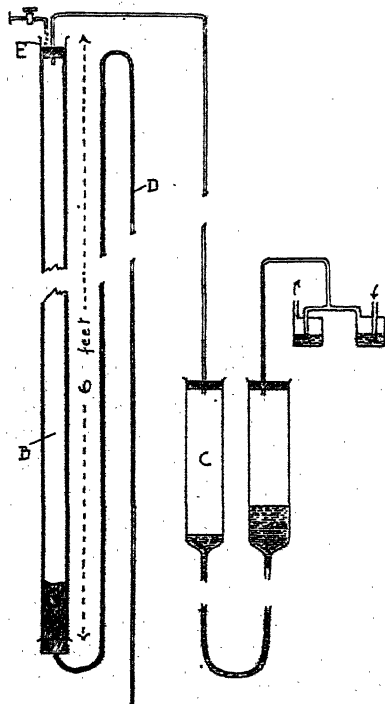
IN the method of preparation of ethylene bromohydrin described by Read and Williams (J., 1917, **111**, 240) and Read and Brook (J., 1920, **117**, 359, 1214), bromine is carried over into the reaction chamber in the form of vapour by a current of air. This has several disadvantages. The ethylene becomes considerably diluted by the air, and a great deal is carried away, so that of the total amount used, only one-third is absorbed. Furthermore, the supply of bromine is not easily regulated.

These disadvantages can be obviated by dropping the bromine from a small, finely-pointed burette down a guide-tube of small bore, the lower part of which reaches to the bottom of the reaction vessel, and is placed as far as possible from the ethylene inlet. The bromine can thus be introduced slowly and, with an efficient stirrer, it becomes dissolved in the water before contact with gaseous ethylene is possible. The yields obtained in two experiments coincided with the average of those obtained by Read and Brook

(*loc. cit.*, p. 1214), while the quantity of ethylene used was only slightly in excess of that absorbed. [Received, January 12th, 1926.]

*An Automatic Siphonic Gas Circulator.* By GEORGE M. GREEN.

THE apparatus described is the result of an unsuccessful attempt to construct a gas-circulating device of the type communicated by Pearson and Thomas (J., 1925, 127, 2450). It does not contain a mechanical device of the plunger variety, and the advantages claimed for it are simplicity of construction and perfect continuity of action, once started. Its disadvantages lie in its comparative slowness and its well-defined intermittency. For certain kinds of laboratory work, however, the latter might recommend themselves.



The apparatus consists of two concentric glass tubes, *B* and *E*, about 6 feet long, one of which slides within the other, the annular space between them being about 1 mm. The inner tube, about 1 inch in internal diameter, is sufficiently heavy to resist the upward-moving tendency produced by the developing hydrostatic pressure. The siphon tube, the length of which can be varied by means of rubber tubing, should be of the greatest possible diameter con-

sistent with rapid and efficient siphonage, and be placed at a suitable height above the working bench. The inflowing water, preferably under a constant pressure head, requires careful regulation at the commencement. The diameter of the upper portions of the U-tube, *C*, containing the oscillating mercury is 2 inches. The valves are of the ordinary mercury seal type. With this apparatus, a constant circulation of at least 50 c.c. of gas per minute is obtainable.—

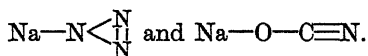
TECHNICAL COLLEGE, HUDDERSFIELD. [Received, December 28th, 1925.]

# LXV.—*A Comparison of Some of the Physical Properties of the Alkali Cyanates and Azides.*

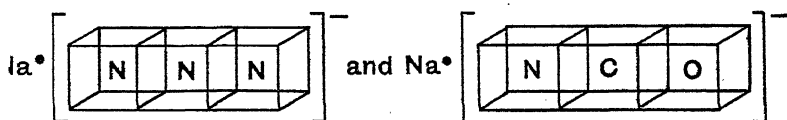
By JOHN ARNOLD CRANSTON and ALEXANDER YOUNG  
LIVINGSTONE.

ACCORDING to modern ideas of the structure of atoms, the chemical and physical properties of elements depend on the number and arrangement of the outer electrons of the atom of the element.

The cyanate and azide ions have the same number of external electrons in their alkali salts, and it is possible that these electrons are arranged in the same way. According to the older views of valency, however, it was more common to find a ring structure assigned to azides and a straight-chain structure to cyanates. The constitutional formulæ were thus represented as



The appearance of these formulæ does not suggest any close resemblance between the physical properties of the compounds. The formulæ suggested by the octet theory for these compounds are



and their great similarity suggests a close resemblance of the physical properties of these two salts. As far as previously published data go, the evidence favours the formulæ of the octet theory, and it was the object of this investigation to supplement the data, which were rather meagre.

*Preparation of Salts.*—The following salts were prepared and purified according to the recognised text-book methods: Potassium cyanate, potassium azide; sodium cyanate, sodium azide.

*Investigation of Physical Properties.*—1. *Densities of solutions.* Since comparative, rather than absolute, values for the data for the various physical properties were aimed at, great care was taken to carry out all measurements for the cyanates and azides under uniform conditions.

A pycnometer of about 17 c.c. capacity was used for the determination of the densities of the solutions that were made up. Cyanates are decomposed by water, but the rate of decomposition

is greatly reduced in presence of alcohol. The solvent employed for the various dilutions was accordingly a mixture of about equal volumes of alcohol and water. All measurements were carried out after the pycnometer containing the solutions had been immersed in a thermostat at 16° for 20 minutes. The results are in Table I.

2. *The refractive indices of the various solutions* were determined by the Abbé refractometer at the same temperature at which their densities had been observed. The results are also in Table I.

TABLE I.

Strength of soln.	Density.		Refractive index.		Density.		Refractive index.	
	KN <sub>3</sub> soln.	KCNO soln.	KN <sub>3</sub> soln.	KCNO soln.	NaN <sub>3</sub> soln.	NaCNO soln.	NaN <sub>3</sub> soln.	NaCNO soln.
N	—	—	—	—	0.979	0.978	1.371	1.374
N/2	0.956	0.956	1.362	1.362	0.954	0.954	1.362	1.364
N/4	0.948	0.948	1.360	1.360	0.946	0.946	1.359	1.360
N/8	0.941	0.941	1.359	1.359	0.941	0.941	1.351	1.352
N/16	0.938	0.938	1.357	1.358	—	—	—	—

3. *The densities of the crystalline salts* were determined by immersing a weighed quantity, about 5 g., in benzene contained in an ordinary specific gravity bottle. Previous experiment had shown that the solubility of these salts in benzene at room temperature is less than 0.1 g. in 100 c.c. Too great reliance cannot be placed on the value obtained for sodium cyanate, owing to the instability of this salt; although different determinations gave consistent values, there was always a detectable quantity of carbonate formed during the measurements. The mean values obtained were as follows:

TABLE II.

	KN <sub>3</sub> .	KCNO.	NaN <sub>3</sub> .	NaCNO.
Density at 20° .....	2.056	2.056	1.846	1.937

4. *Determination of solubilities.* The solubilities of these salts in alcohol ( $d^{20}_4$  0.799) were determined at 0° and at the boiling point of the saturated solution. Definite volumes of the solutions were withdrawn by means of a pipette, and the solutions weighed. The cyanates were estimated volumetrically by the method suggested by Masson (*Chem. News*, 1906, 90, 5, 17), the azides by the method suggested by Raschig (*Chem. Ztg.*, 1908, 1203).

Solubilities were also measured in 20% water and 80% alcohol at 0° and at the boiling point of the saturated solution, and as well as in benzene at the boiling point.

TABLE III.

Solvent.	Weight dissolved in 100 g. of solvent.			
	KN <sub>3</sub> .	KCNO.	NaN <sub>3</sub> .	NaCNO.
Alcohol at 0° .....	0.16	0.16	0.22	0.22
Alcohol at b. p. ....	0.54	0.53	0.46	0.52
80% Alcohol } at 0° .....	1.8	1.9	—	—
20% Water } .....				
" " } at b. p. ....	5.9	6.2	—	—
Benzene at b. p. ....	0.15	0.18	0.10	0.13

5. *Conductivity of solutions.* A preliminary attempt to determine the hydron concentration of a solution of an alkali azide by the electrometric method showed that the salt is decomposed by water in presence of platinum black. This decomposition is very rapid when hydrogen is present occluded in the platinum. Nitrogen and ammonia are liberated, and the solution becomes progressively more alkaline. Apparently the reaction is as follows:  $3\text{KN}_3 + 3\text{H}_2\text{O} = 3\text{KOH} + 4\text{N}_2 + \text{NH}_3$ .

Since cyanates are also decomposed by water, the solvent used in the conductivity measurements was methyl alcohol ( $d^{20}$  0.789).

The following results were obtained.

TABLE IV.

Strength of solution.	Equivalent conductivity at 25°.			
	NaN <sub>3</sub> .	NaCNO.	KN <sub>3</sub> .	KCNO.
N/10	58.7	58.3	62.8	60.3
N/20	69.0	68.0	68.0	68.6
N/40	78.8	75.6	77.2	77.6
N/80	90.4	88.0	88.8	88.8

The investigations of Carrara (*Gazzetta*, 1896, 26, i, 134) have shown that the ionic conductivities of sodium and potassium are approximately equal in methyl alcohol.

### Discussion of Results.

It will be seen from the above tables that all the physical properties investigated have shown the great resemblance between sodium azide and sodium cyanate on the one hand and potassium azide and potassium cyanate on the other. This, taken in conjunction with the similarity of crystal structure noted by Langmuir (*J. Amer. Chem. Soc.*, 1919, 41, 1543), is strong evidence that the arrangement of electrons and atoms in the cyanate and azide ions is the same.

ROYAL TECHNICAL COLLEGE, GLASGOW. [Received, October 31st, 1925.]

LXVI.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part VI. Rotatory Powers of Phenyl, o, m, p-Tolyl and  $\beta$ -Naphthyl Derivatives of d-Camphorimide and d-Camphoramic Acid.*

By BAWA KARTAR SINGH and AMAR NATH PURI.

THE rotatory powers of a number of aryl derivatives of *d*-camphorimide and *d*-camphoramic acid in three solvents at different concentrations have been studied with the object of finding some relation between their optical activity and chemical constitution, and the following conclusions drawn :

1. Substitution of an aryl group for the imido-hydrogen atom increases the rotatory power, and more so than does substitution of the benzyl group (Singh and Biswas, J., 1924, 125, 1895).

2. The influence of the solvent on the rotatory power is considerable in the case of derivatives of *d*-camphoramic acid, but it is small in the case of those of *d*-camphorimide.

The order of the dielectric constants of the solvents employed is methyl alcohol (32.5) > ethyl alcohol (26.0) > acetone (21.2). In most cases (see Tables I and II), the order of the rotatory powers in these solvents is methyl alcohol > ethyl alcohol > acetone. It thus appears that in the case of these solvents the order of the rotatory powers generally runs parallel to their dielectric constants, although there is no direct proportionality between them.

3. The relative magnitude of the rotatory powers of phenyl and tolyl derivatives of *d*-camphorimide and *d*-camphoramic acid varies with the nature of the solvent and the concentration of the solution, as is seen in Tables I and II.

TABLE I.

Derivatives of <i>d</i> -camphoramic acid.	2% Solution.			1% Solution.		
	EtOH.	MeOH.	Me <sub>2</sub> CO.	EtOH.	MeOH.	Me <sub>2</sub> CO.
Phenyl	+131°	+150°	+101°	+133°	+152°	+101°
<i>o</i> -Tolyl	144	146	98	158	151	91
<i>m</i> -Tolyl	118	140	89	122	147	92
<i>p</i> -Tolyl	144	167	120	146	170	122

*o* = *p* > *un.* > *m*; *p* > *un.* > *o* > *m*; *p* > *un.* > *o* > *m*; *o* > *p* > *un.* > *m*; *p* > *un.*, *o* and *m*; *p* > *un.* > *m* and *o*.

For none of these derivatives do Frankland's and Cohen's rules hold.

TABLE II.

Derivatives of <i>d</i> -camphorimide.	1.5% Solution.			0.75% Solution.		
	EtOH.	MeOH.	Me <sub>2</sub> CO.	EtOH.	MeOH.	Me <sub>2</sub> CO.
Phenyl	+48°	+49°	+44°	+48°	+52°	+48°
<i>o</i> -Tolyl	45	46	36	53	56	43
<i>m</i> -Tolyl	48	48	50	55	53	37
<i>p</i> -Tolyl	46	52	54	42	48	49

In the case of the derivatives of *d*-camphorimide, the differences in the rotatory powers of the position isomerides are in many cases so small, and within the limits of experimental error, that it is not permissible to draw any general conclusions.

The variation of the optical rotatory power with concentration was more fully investigated in the case of *d*-camphor-*p*-tolylamic acid in ethyl and methyl alcohols for concentrations varying from 1 to 10%. In both solvents the rotatory power decreases as the concentration increases. This may be due to the decrease in the number of optically active molecules in more concentrated solutions owing to molecular association.

4. The rotatory power of a cyclic compound is usually considerably greater than that of the corresponding open-chain derivative. Thus the rotatory powers of esters of 1-methyl-3-cyclopentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyladipic acid (Haller, *Compt. rend.*, 1905, 140, 1205), and the hexahydrophthalic acids have much lower rotatory powers than their anhydrides (Werner, *Ber.*, 1899, 32, 3046). This rule is more strikingly borne out in the case of derivatives of monosaccharides. The rotatory power of *d*-mannitol is  $[\alpha]_D^{20} = -0.2^\circ$  (Fischer, *Ber.*, 1890, 23, 3684), whereas that of *d*-mannonolactone is  $+53.8^\circ$  (Fischer, *Ber.*, 1889, 22, 3219). The high rotatory power of most of the sugars as compared with the corresponding polyhydric alcohols is a proof of the ring structure of the former. The increase which is brought about in the rotatory power of sugar alcohols by boric acid is attributed to the formation of ring complexes. Camphoramides and their anhydrides form an exception to the rule, the acids having  $[M]_D$  89.45° ( $\alpha$ ), 119.4° ( $\beta$ ) in ethyl alcohol, whilst the anhydride has  $[M]_D$  10.99°. It was pointed out (J., 1924, 125, 1895) that opening the rings of *d*-camphorimide and its derivatives increases the rotation considerably; e.g. the following are values of  $[M]_D$  in ethyl alcohol: camphorbenzylimide 30.19°, camphorbenzylamic acid 99.88°, camphor-*m*-nitrobenzylimide 31.92°, camphor-3-nitrobenzylamic acid 106.7°. The differences in the molecular rotatory powers of the aryl derivatives

of *d*-camphorimide and *d*-camphoramidic acid are of the same order as of the foregoing substances, except in the case of  $\beta$ -naphthyl derivatives, for which the difference is much greater; e.g., the following are values of  $[M]_D$  in ethyl alcohol: camphor- $\beta$ -naphthylimide 60°, *d*-camphor- $\beta$ -naphthylamidic acid 229°. From the foregoing instances it may be concluded that when an open-chain, optically active compound is transformed into a ring compound, there is a marked change (not necessarily an increase) in the rotatory power.

#### EXPERIMENTAL.

*Aryl Derivatives of d-Camphoramidic Acid.*—*d*-Camphorphenylamidic acid,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NHPh}$ , was prepared by heating camphoric anhydride and aniline in molecular proportions in chloroform on the water-bath for 4–5 hours. The solid obtained on cooling crystallised from aqueous alcohol in needles, m. p. 209–210°. Auwers and Schleicher (*Annalen*, 1899, **309**, 341) give m. p. 203–204°.

*d*-Camphor-*p*-tolylamidic acid,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , was prepared like the foregoing substance as leaflets, m. p. 214–215°. Wootton (J., 1910, **97**, 405), who obtained it by heating an intimate mixture of camphoric anhydride and the substituted amine for a few minutes at 150–180°, gives the melting point 212–214°, whereas Abati and Notaris (*Gazzetta*, 1909, **39**, ii, 219) give 201–209°.

*d*-Camphor-*m*-tolylamidic acid was prepared by Wootton's method (*loc. cit.*) and purified by dissolving it in alcohol and adding animal charcoal. It was recrystallised as needles, m. p. 208–209°.

*d*-Camphor-*o*-tolylamidic acid, prepared in the foregoing way, melted at 196–197°.

*d*-Camphor- $\beta$ -naphthylamidic acid,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , was prepared by both methods as white leaflets, m. p. 212–213°. The yield was, however, better when the condensation was carried out without any solvent.

*N-Aryl Derivatives of d-Camphorimide.*—These compounds were prepared by heating camphoric anhydride and the substituted amines in molecular proportions with the addition of a little anhydrous sodium sulphate in an oil-bath (215–230°) for 2 to 3 hours. The products of condensation were extracted with alcohol, decolorised by animal charcoal, and precipitated by adding water. They were twice recrystallised from aqueous alcohol, and gave the following melting points: phenyl, 117–118°; *o*-tolyl, 105–106°; *m*-tolyl, 121–122°; *p*-tolyl, 127–128°;  $\beta$ -naphthyl, 171–172°.

The tolyl and  $\beta$ -naphthyl derivatives of camphorimide were prepared by Wootton (*loc. cit.*) by boiling a solution of the corresponding *N*-substituted *d*-camphoramidic acid in glacial acetic acid with acetyl chloride for 2 hours. Wootton gives the melting point



TABLE III.

Solvent.	Conc. (g./100 c.c.).	Temp.	$\alpha_D$ .	$[M]_D$ .	Conc. (g./100 c.c.).	Temp.	$\alpha_D$ .	$[M]_D$ .
<i>d</i> -Camphorphenylamic acid.					<i>d</i> -Camphorphenylimide.			
EtOH	0.5265	26°	+0.51°	+133°	0.7693	18°	+0.29°	+48°
"	1.0516	27	1.00	131	1.4950	19	0.56	48
MeOH	1.0025	22	1.11	152	0.7447	18	0.30	52
"	2.0030	22	2.19	150	1.4765	17	0.56	49
Me <sub>2</sub> CO	0.9775	23	0.72	101	0.7457	17	0.28	48
"	2.0230	24	1.47	100	1.4755	18	0.50	44
<i>d</i> -Camphor- <i>o</i> -tolylamic acid.					<i>d</i> -Camphor- <i>o</i> -tolylimide.			
EtOH	1.0155	26	1.11	158	0.7618	18	0.30	53
"	2.0345	24	2.03	144	1.4925	19	0.49	45
MeOH	1.0140	22	1.06	151	0.6807	17	0.28	56
"	1.9995	22	2.02	146	1.1772	18	0.40	46
Me <sub>2</sub> CO	0.9099	22	0.57	91	0.6607	17	0.21	43
"	2.0701	23	1.40	98	1.4585	17	0.39	36
<i>d</i> -Camphor- <i>m</i> -tolylamic acid.					<i>d</i> -Camphor- <i>m</i> -tolylimide.			
EtOH	1.0210	23	0.86	122	0.7678	18	0.31	55
"	1.9710	25	1.61	118	1.5135	19	0.53	48
MeOH	1.0130	22	1.03	147	0.7187	17	0.28	53
"	1.7292	22	1.68	140	1.4374	18	0.51	48
Me <sub>2</sub> CO	1.0325	22	0.66	92	0.5906	17	0.16	37
"	2.0340	23	1.25	89	1.4565	18	0.54	50
<i>d</i> -Camphor- <i>p</i> -tolylamic acid.					<i>d</i> -Camphor- <i>p</i> -tolylimide.			
EtOH	0.9970	27	1.01	146	1.0030	23	0.31	42
"	1.9965	27	1.99	144	2.0070	24	0.68	46
"	2.8994	17	2.91	145				
"	4.0040	17	3.92	142				
"	5.0140	17	4.86	140				
"	5.9710	18	5.70	138				
"	7.0395	18	6.58	135				
"	8.0981	17	7.50	134				
"	9.0550	18	8.16	130				
"	10.0560	18	8.95	129				
MeOH	1.0035	22	1.18	170	0.7673	18	0.27	48
"	2.0070	22	2.32	167	1.4580	17	0.56	52
"	3.0130	18	3.40	163				
"	4.0100	19	4.49	162				
"	5.0671	17	5.26	150				
"	10.0360	17	10.10	145				
Me <sub>2</sub> CO	0.9510	24	0.80	122	0.7708	18	0.28	49
"	2.0250	22	1.68	120	1.4700	18	0.59	54
<i>d</i> -Camphor- $\beta$ -naphthylamic acid.					<i>d</i> -Camphor- $\beta$ -naphthylimide.			
EtOH	1.1505	14	1.62	229	0.9130	13	0.37	60
MeOH	1.0180	14	1.54	246	0.5100	15	0.21	61
Me <sub>2</sub> CO	1.0530	15	1.38	213	0.8520	15	0.32	56

for the *o*-tolyl derivative 195—196°, which is obviously wrong. We also prepared this substance by his method and found the melting point 105—106°.

Before their rotatory powers were determined, the compounds were recrystallised three times in order to ensure their "optical" purity. Wootton has recorded the rotatory powers of these sub-

stances in acetone; his exact concentrations are not stated. In the case of derivatives of camphoramic acid, his values agree with ours, except in the case of the *p*-tolyl derivative, his value (107°) being lower than ours (120° to 122°, according to concentration). In the case of the *p*-tolyl derivative of *d*-camphorimide, his value ( $[\alpha]_D^{34}$ ) is again lower than ours (49° to 54°, according to concentration).

The rotatory powers recorded in Table III were determined by dissolving a given weight of the substance in a solvent, and making up the solution to a definite volume. The readings were taken in a 2-dm. tube within 45 minutes of making up the solution. There was no mutarotation.

The rotatory powers and dispersion ratios of *d*-camphorbenzylamic acid and *d*-camphor-*m*-nitrobenzylamic acid (higher-melting form) were omitted from Part V of this series (*loc. cit.*). They are given below for the sake of completeness.

Solvent.	Conc. (g./100 c.c.).	Temp.	Molecular rotatory powers.			Dispersion ratios.
			$[M]_{5893}$	$[M]_{5780}$	$[M]_{5461}$	$\alpha_{5461}/\alpha_{5893}$
<i>d</i> -Camphorbenzylamic acid.						
Chloroform .....	1.6193	23°	+92°	+95°	+108°	1.18
Acetone.....	1.9143	25	97	98	111	1.15
Ether.....	1.1590	21	89	92	107	1.21
Ethyl alcohol .....	3.3400	22	100	107	120	1.25
Methyl alcohol ...	1.2249	23	93	98	115	1.23
<i>d</i> -Camphor- <i>m</i> -nitrobenzylamic acid, m. p. 179°.						
Chloroform .....	2.0485	23	80	83	94	1.18
Acetone.....	2.0676	25	95	97	111	1.13
Ethyl alcohol .....	2.8900	22	107	116	140	1.29
Methyl alcohol ...	1.5784	23	109	112	127	1.16

We wish to thank Mr. Sher Singh, B.Sc., for determining the rotatory powers of the  $\beta$ -naphthyl derivatives.

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[Received, October 24th, 1925.]

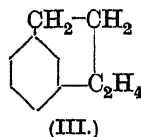
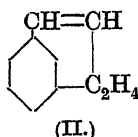
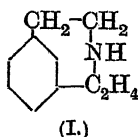
## LXVII.—Conditions of Formation of Rings Attached to the *o*-, *m*-, and *p*-Positions of the Benzene Nucleus. Part II. The Reduction of *m*- and *p*-Phenylene-diacetonitrile.

By ALAN FRANCIS TITLEY.

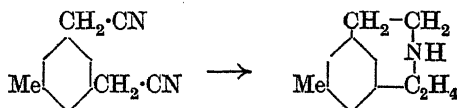
IN the course of some work on ring formation, the scope of which is outlined in Part I of this series (J., 1922, 121, 1562), and a further account of which will be published shortly, it was found desirable

to repeat some investigations recently carried out by von Braun and his collaborators.

While attempting to prepare *m*-phenylene- $\beta\beta'$ -diethylamine by the reduction of *m*-phenylenediacetonitrile with sodium and alcohol, von Braun, Karpf, and Garn (*Ber.*, 1920, 53, 98) claimed to have isolated a secondary amine of the composition  $C_{10}H_{13}N$ , to which they assigned the structure (I), where the heterocyclic ring is joined to the benzene nucleus in the meta-position. From this amine, by thermal decomposition of the quaternary dimethylammonium hydroxide with loss of dimethylamine and water, they stated that they obtained an unsaturated hydrocarbon and, by further reduction, a saturated hydrocarbon, to which they assigned the structures (II) and (III), respectively.



More recently, von Braun and Engel (*Ber.*, 1925, 58, 281) have described a homologue of this type, obtained in a similar manner by reducing 5-methyl-1 : 3-phenylenediacetonitrile.



The remarkable ease with which examples of this meta-ring system, generally supposed to be incapable of existence, are formed, together with their close structural relationship to the products it was hoped to obtain by the action of sodium on *m*-phenylene-diacetic ester (Part I, *loc. cit.*), rendered a re-examination of this work desirable. It was not found possible, however, to confirm the results of von Braun and his co-workers and, in the present paper, evidence is brought forward to show that the amine (I) described by von Braun, Karpf, and Garn (*loc. cit.*) is in reality  $\beta$ -*m*-tolylethylamine (VII), and the unsaturated hydrocarbon derived from it *m*-methylstyrene (IX).\*

The reduction of *m*-phenylenediacetonitrile, when carried out in accordance with the directions of these authors and using the same quantities and conditions, led to the formation of a mixture

\* The proof of this paper was sent to Professor von Braun, and he wishes me to say that he has been engaged for some time in repeating the researches in question and has arrived at results which are identical with those contained in the present communication.—W. H. PERKIN.

of products, basic and non-basic. The non-basic substances were removed, together with the excess of alcohol, by steam-distillation of the acidified reaction mixture. These proved to be *m*-tolyl-acetonitrile (IV), which was identified by conversion into the beautifully crystalline amide, m. p. 141° (compare Radziszewski and Wispek, *Ber.*, 1885, **18**, 1281), *m*-xylene (V), identified by b. p. and analysis, and a little unchanged *m*-phenylenediacetonitrile. Considerable quantities of free hydrocyanic acid could also be detected.

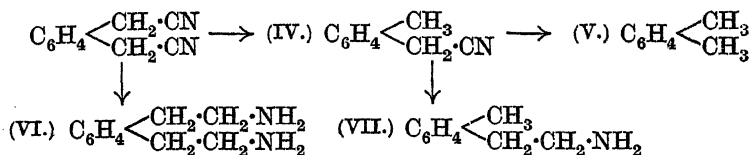
The basic products, after liberation from the acid solution by excess of sodium hydroxide, proved to be a mixture of *m*-phenylene- $\beta\beta'$ -diethylamine (VI), b. p. 162°/18 mm., formed in accordance with the observation of von Braun in a 10–15% yield, and a monoamine of b. p. 97–98°/15 mm., obtained in about 40% yield, which appeared to be identical with the substance  $C_{10}H_{13}N$  described by von Braun as a secondary amine.

This monoamine gave a hydrochloride, which crystallised in large, glistening leaflets of m. p. 160°, a sulphur-yellow picrate, m. p. 174°, a benzoyl derivative, m. p. 72°, a phenylthiocarbamide, m. p. 86–87°, a platinum salt which, after blackening between 230° and 240°, melted with vigorous decomposition at 246°, and a quaternary methiodide, m. p. 237°. (The substance described by von Braun as a secondary amine had in almost every respect the same properties, viz., b. p. 97–98°/16 mm., the hydrochloride, m. p. 160°, the picrate, m. p. 176°, the benzoyl derivative, m. p. 72°, the phenylthiocarbamide, m. p. 87°, the platinum salt, m. p. 232°, and the quaternary methiodide, m. p. 236°.)

The amine, however, prepared in this way, did not give analytical results corresponding to the composition  $C_{10}H_{13}N$ , but invariably showed a higher hydrogen content. It was at first thought that it had the composition  $C_{10}H_{15}N$ , but careful analyses of several samples, including one prepared from the recrystallised hydrochloride, clearly suggested the composition  $C_9H_{13}N$ .

On treating a solution of the base in dilute hydrochloric acid with sodium nitrite, a brisk evolution of nitrogen occurred and a pale yellow oil separated. This oil, which had a characteristic pungent and rather sweet odour, dissolved readily in ether and, after shaking with dilute sodium carbonate to remove nitrous acid, gave no response to the Liebermann test.

In view of these results and the nature of the non-basic products of the reaction, it seems quite clear that the normal reduction of *m*-phenylenediacetonitrile to the diamine (VI) is largely accompanied by the conversion of first one and then the other  $-CH_2-CN$  group into  $-CH_3$  groups, the intermediate stage being itself reduced to a monoamine. The process is best made clear by the following scheme:



The monoamine described above, although evidently identical, except in its behaviour towards nitrous acid, with the monoamine (I) of von Braun, is in reality  $\beta$ -*m*-tolylethylamine (VII).

In order to establish the identity of the monoamine beyond question,  $\beta$ -*m*-tolylethylamine was prepared by the reduction of *m*-tolylacetonitrile (IV) with sodium and alcohol. Using approximately twice the theoretical quantity of reducing agent, a yield of about 50% of  $\beta$ -*m*-tolylethylamine was obtained, practically the whole of the rest of the nitrile being reduced to *m*-xylene.

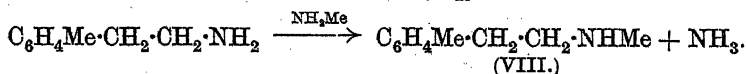
The amine had b. p. 216°/762 mm. and 98°/15 mm. and gave a hydrochloride, m. p. 160°, and a picrate, m. p. 174°, in accordance with the observations of Sommer (*Ber.*, 1900, **33**, 1079).

The benzoyl compound, phenylthiocarbamide, and quaternary methiodide also had the same melting points as the corresponding compounds, prepared from the specimen of monoamine which had been obtained by reducing *m*-phenylenediacetonitrile. There was no depression of the m. p. on mixing samples of these derivatives.

This reduction of the  $-\text{CH}_2 \cdot \text{CN}$  group to  $-\text{CH}_3$ , although apparently of rare occurrence, is not unknown, and a few instances are recorded in the literature—for example, the reduction of cyanomethylbenziminazole to methylbenziminazole with sodium and alcohol (Bloch, *J. Soc. Chem. Ind.*, 1919, **38**, 118).

$\beta$ -*m*-Tolylethylamine combines readily with piperonal, the condensation product crystallising well and melting at 53–54°. After being heated in a sealed tube with a slight excess of methyl iodide and then decomposed with aqueous alcohol, the latter yields  $\beta$ -*m*-tolylethylmethylamine hydriodide, m. p. 104°, from which the free base (VIII) was obtained, b. p. 88°/12 mm.

This base was prepared because of the very definite statement made by von Braun regarding the secondary nature of his monoamine. It was thought possible that interaction might occur between  $\beta$ -*m*-tolylethylamine and methylamine, formed by reduction of the free hydrocyanic acid present during the reaction, with the formation of  $\beta$ -*m*-tolylethylmethylamine (VIII), and that this secondary amine ( $\text{C}_{10}\text{H}_{15}\text{N}$ ), in itself and in its derivatives, might closely resemble the primary amine ( $\text{C}_9\text{H}_{13}\text{N}$ ).

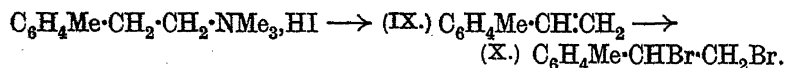


This, however, was not found to be the case, since the secondary amine gave a hydrochloride extremely soluble in alcohol and most other solvents, which, when crystallised from chloroform-ligroin, had m. p. 134°. The picrate had m. p. 127°, whilst the benzoyl compound was an oil which could not be induced to crystallise.

No evidence of the formation of any secondary amine by the reduction of *m*-phenylenediacetonitrile was forthcoming, and since the properties of  $\beta$ -*m*-tolylethylamine and its derivatives agree in almost every respect with those of the monoamine described by von Braun, there seems little doubt that the two are identical.

As previously mentioned, von Braun, Karpf, and Garn found that the quaternary ammonium hydroxide of their base, on distillation, lost dimethylamine and water with the formation of an unsaturated hydrocarbon,  $C_{10}H_{10}$  (II), which had b. p. 62–63°/18 mm. and added two atoms of bromine with the formation of a dibromide, m. p. 48°.

It was found that the quaternary methiodide of  $\beta$ -*m*-tolylethylamine, on boiling with methyl-alcoholic potash, lost trimethylamine (identified by means of the picrate and platinum salt), with the formation of *m*-methylstyrene (IX), b. p. 62°/18 mm., which by the addition of two atoms of bromine gave the corresponding dibromide (X), m. p. 47° (Müller, *Ber.*, 1887, 20, 1216, found m. p. 45°).



The hydrocarbon described by von Braun is stated to have an abnormally low density ( $d^{20}_4$  0.900) as compared with "the isomeric hydrocarbons 3-methylindene ( $d$  0.968) and  $\Delta^1$ -dihydronaphthalene ( $d$  0.997)," whilst it resembled a styrene in polymerising under the action of light. The density of *m*-methylstyrene was found to be 0.906 at 16° and its tendency to polymerise has been noted by previous workers (Müller, *loc. cit.*).

The saturated hydrocarbon (III) prepared by von Braun had the low density  $d^{20}_4$  0.852 as compared with 1-methylhydrindene ( $d$  0.966) and 1:2:3:4-tetrahydronaphthalene ( $d$  0.968), whilst the refractive index was  $n^{20}_D = 1.497$ .

The reduction of *m*-methylstyrene to *m*-tolylethane was not investigated, but it may be noted that the density of the latter is recorded by Wroblewski (*Annalen*, 1878, 192, 198) as 0.869 at 20°. The refractive index of *m*-tolylethane has not apparently been measured, but that of the isomeric *p*-tolylethane is stated to have the value  $n^{20}_D = 1.494$  (Klages and Keil, *Ber.*, 1903, 36, 1637).

*Reduction of p-Phenylenediacetonitrile.*

The reduction of *p*-phenylenediacetonitrile with sodium and alcohol was also investigated. In this case, the  $-\text{CH}_2\cdot\text{CN}$  groups are reduced to methyl groups even more readily than those in the *m*-isomeride, a yield of about 50% of  $\beta$ -*p*-tolylethylamine being obtained. The rest of the nitrile was almost wholly reduced to *p*-xylene, whilst no appreciable quantity of *p*-phenylene- $\beta\beta'$ -diethylamine was formed.

The identity of the monoamine was again established by reducing *p*-tolylacetonitrile, which yielded the same product.

$\beta$ -*p*-Tolylethylamine has b. p.  $94-95^\circ/13$  mm. and absorbs carbon dioxide rapidly from the air. It forms a sparingly soluble hydrochloride, m. p.  $216^\circ$  (compare Ciesielski, *Anzeiger Akad. Wiss. Krakau*, 1906, 270; *Centr.*, 1907, I, 1793). On treatment with nitrous acid, it passes into an alcohol, which has the same characteristic sweet odour as that derived from  $\beta$ -*m*-tolylethylamine. This  $\beta$ -*p*-tolylethyl alcohol boils at  $112^\circ/12$  mm. and combines with *p*-nitrobenzoyl chloride, yielding an ester which crystallises well and melts at  $91^\circ$ .

The amine forms a *picrate*, m. p.  $155^\circ$ , a platinum salt, m. p.  $234^\circ$ , a *benzoyl* derivative, m. p.  $89^\circ$ , and a quaternary *methiodide*, m. p.  $244^\circ$ . With piperonal, it forms a beautifully crystalline condensation product, m. p.  $107^\circ$ , which, by treatment with methyl iodide in the manner already described, is converted into  $\beta$ -*p*-tolylethylmethylamine hydriodide, m. p.  $149^\circ$ . The free base obtained from this had b. p.  $96^\circ/12$  mm. and yielded a readily soluble hydrochloride, m. p.  $191^\circ$ , a *picrate*, m. p.  $135^\circ$ , and an oily benzoyl compound.

The quaternary methiodide of the base, on boiling with methylalcoholic potash, was converted into *p*-methylstyrene, b. p.  $59-60^\circ/12$  mm., which yielded a dibromide, m. p.  $45-46^\circ$  (compare Klages and Keil, *loc. cit.*).

No evidence of any ring formation was obtained during these experiments.

## EXPERIMENTAL.

$\omega\omega'$ -Dibromo-*m*-xylene.—The bromination of *m*-xylene to the  $\omega\omega'$ -dibromo-compound was studied under various conditions, but the best results were obtained by following the directions of Atkinson and Thorpe (*J.*, 1907, 91, 1696). In this method, *m*-xylene is treated with rather more than the theoretical quantity of bromine required for monobromination, and the mixture of mono- and di-bromoxylenes separated by fractional distillation.

*m*-Xylene (200 g.) was treated at  $130^\circ$ , under reflux, with dry

bromine (405 g.) during about 6 hours. The product was freed from hydrogen bromide by 2 days' standing over solid caustic soda in a vacuum desiccator. The bulk of the monobromoxylene passed over at 110—115°/20 mm., and when the temperature reached 125° the distillation was stopped and the residue in the flask, which solidified almost completely on cooling, was broken up on a Büchner funnel, washed with a little low-boiling ligroin, and recrystallised from acetone. Large, colourless prisms, m. p. 76°, were obtained. The yield of dibromo-compound is about 35%.

The  $\omega$ -monobromoxylene was refractionated through a column, and the fraction 100—101°/14 mm. collected and used for the preparation of *m*-tolylacetonitrile (see later). The yield of monobromide is about 45% (Found: Br, 43.0. Calc., Br, 43.2%).

$\omega\omega'$ -Dibromo-*p*-xylene.—The bromination of *p*-xylene was carried out in the same manner as the above, using a quantity of bromine equal to twice the weight of the *p*-xylene taken. The reaction product solidified completely, and after pressing on a porous plate was extracted with ligroin (b. p. 40—50°) in a Soxhlet apparatus, which dissolved all the monobromide. The crude dibromo-compound crystallised from a small volume of warm chloroform in compact clusters of prisms, m. p. 143—144°.

The monobromo-compound, obtained by evaporation of the ligroin extract, after another crystallisation from the same solvent, separated in very long, colourless needles, m. p. 35.5°.

*m*-Phenylenediacetonitrile.—The conversion of the dibromoxylenes into the corresponding nitriles is usually attended by side-reactions leading to the formation of oily or amorphous by-products. These effects are minimised if the reaction is carried out as rapidly as possible, and the following method was found, in the case of dibromo-*m*-xylene, to give practically quantitative results.

A boiling solution of potassium cyanide (50 g.) in water (110 g.) and ethyl alcohol (350 c.c.) is rapidly stirred mechanically while finely powdered dibromo-*m*-xylene (88 g.) is added as rapidly as the violence of the reaction will permit. The hot solution is filtered at once from traces of brown, amorphous material. A litre of water is then added and the nitrile extracted with ether, dried, and distilled. The nitrile boiled at 230—231°/20 mm. and solidified, on cooling, to a snow-like mass of needles, m. p. 27°. Yield, 47 g.

*m*-Tolylacetonitrile.—Monobromo-*m*-xylene (128 g.) was treated with potassium cyanide (49 g.) dissolved in a mixture of water (120 g.) and alcohol (400 c.c.) in exactly the same manner as the above. The nitrile (yield about 85%) boiled at 245—247°/745 mm. with slight decomposition (compare Radziszewski and Wispek,



*loc. cit.*) and was better distilled under reduced pressure; it then had b. p.  $133^{\circ}/15$  mm.

*p-Phenylenediacetonitrile*.—The nitrile was prepared in the same manner as the meta-isomeride, the same quantities and conditions being used. The maximum possible yield, however, seems to be about 70%. The remainder of the bromo-derivative is converted into a bright yellow, infusible, amorphous, highly insoluble product, which does not appear to contain any nitrogen or halogen and was not further investigated. The nitrile separates from alcohol in colourless prisms, m. p.  $96^{\circ}$ .

*p-Tolylacetonitrile*.—This nitrile was obtained from monobromo-*p*-xylene by the usual method. It was found necessary in this case to boil the reaction mixture for a short time to complete the conversion. The nitrile has b. p.  $135^{\circ}/14$  mm. and solidifies in ice to a white mass which melts at  $17^{\circ}$ .

*Reduction of m-Phenylenediacetonitrile*.—Sodium (36.8 g.) in the form of small chips was placed in a 3-litre flask, closed with a cork through which passed an air condenser about 4 feet in length and  $1\frac{1}{2}$  inches in diameter. This was itself fitted at the top with a water-condenser. (In some experiments, the sodium was previously granulated under toluene, but this did not appear to affect the yield materially.)

A nearly boiling solution of *m*-phenylenediacetonitrile (14.6 g.) in absolute alcohol (550 g.) was then rapidly added. When the extremely violent reaction had subsided, a solution of 90 g. of concentrated sulphuric acid in 300 c.c. of water was added and the mixture distilled in steam. The acid solution was filtered from traces of a brown, sticky by-product, and, if necessary, extracted with ether. It was then rendered alkaline with caustic soda (30 g.) and thoroughly extracted with ether. After the ethereal solution had been dried with anhydrous magnesium sulphate and the ether removed, 8 g. of a pale yellow oil were obtained, from which 5–6 g. of b. p.  $97$ – $98^{\circ}/15$  mm. or  $101$ – $102^{\circ}/18$  mm. were isolated (Found: C, 80.1, 80.2; H, 9.8, 9.7; N, 10.25.  $C_9H_{13}N$  requires C, 80.0; H, 9.6; N, 10.4%).

The combined aqueous-alcoholic steam distillates from three such experiments were distilled through a column until about three-quarters of the alcohol had been removed. Water was then added to the residue, and the insoluble material extracted with ether. After removal of the ether, about 15 g. of non-basic products were obtained, and from these, by careful fractionation, 8–9 g. of a liquid, b. p.  $138$ – $141^{\circ}/758$  mm., which had a xylene-like odour and burned with a smoky flame (Found: C, 90.1; H, 9.3. Calc. for  $C_8H_{10}$ : C, 90.6; H, 9.4%).

From the residue about 4—5 g. of a liquid, b. p. 138—140°/18 mm., were obtained which, after shaking with dilute hydrogen peroxide and standing over-night, were converted into a crystalline mass. Recrystallised from hot water, the substance formed colourless leaflets, m. p. 141—142°, and analysis left no doubt that it was identical with *m*-tolylacetamide (compare Radziszewski and Wispek, *loc. cit.*) (Found : N, 9.6. Calc. for  $C_9H_{11}ON$  : N, 9.7%).

The amine, b. p. 97—98°/15 mm., described above, absorbed carbon dioxide readily from the air, with the formation of a solid carbonate.

The hydrochloride of the base was readily obtained by passing dry hydrogen chloride into its alcoholic solution. It separated in large, transparent laminae, m. p. 160° (Found : C, 63.4; H, 8.35.  $C_9H_{13}N.HCl$  requires C, 63.0; H, 8.2%).

The picrate, obtained by adding an alcoholic solution of the base to a saturated alcoholic solution of picric acid, formed sulphur-yellow needles, m. p. 174° (176° corr.) (compare Sommer, *loc. cit.*) (Found : N, 15.4. Calc., N, 15.4%).

The platinum salt, which separated in small, orange-brown needles on mixing warm solutions of the hydrochloride of the base and chloroplatinic acid, blackened between 230° and 240° and melted with vigorous decomposition at 246° (von Braun found m. p. 232° for this substance) (Found : Pt, 28.85. Calc. for  $2C_9H_{13}N.H_2PtCl_6$  : Pt, 28.7%).

The benzoyl derivative was best obtained by mixing 1 g. of the hydrochloride with 0.9 g. of benzoyl chloride and adding 15 c.c. of a 5% solution of sodium hydroxide. The sticky, white mass gradually solidified; recrystallised either from a very small volume of alcohol or from alcohol-ligroin, it formed colourless prisms, m. p. 72°.

The phenylthiocarbamide was obtained by boiling a solution of equal weights of the base and of phenylthiocarbimide in alcohol for about 10 minutes and adding ligroin; the thiocarbamide separated in colourless needles, which were recrystallised from a little warm alcohol and then had m. p. 86—87°.

The quaternary methiodide was easily prepared by shaking a mixture of the base (4.5 g.) with methyl iodide (20 g.) and 75 c.c. of a 5% solution of sodium hydroxide. Considerable heat was developed and the quaternary salt was deposited in white crusts. It crystallised from alcohol, in which it was only very moderately soluble in the cold, in colourless prisms, m. p. 237°.

*Reduction of m-Tolylacetonitrile.*—This reduction was carried out in the same apparatus and by the same method as that of the dinitrile already described. Thirty g. of sodium were used to reduce a solution of 15 g. of *m*-tolylacetonitrile in 450 g. of absolute alcohol.

The reaction products were worked up in the same manner, giving a yield of about 7 g. of  $\beta$ -m-tolylethylamine, b. p.  $98^{\circ}/15$  mm. or  $112^{\circ}/25$  mm., and about 5 g. of m-xylene (Found : C, 79.9; H, 9.8; N, 10.2. Calc. for  $C_9H_{13}N$  : C, 80.0; H, 9.6; N, 10.4%).

*Condensation of  $\beta$ -m-Tolylethylamine with Piperonal.*—A mixture of the base (10 g.) with piperonal (11 g.) was warmed on the water-bath for  $\frac{1}{2}$  hour. The product, which solidified on cooling, crystallised from about 100 c.c. of hot alcohol in yellowish-white leaflets, m. p.  $54^{\circ}$  (Found : C, 76.5; H, 6.6.  $C_{17}H_{17}O_2N$  requires C, 76.4; H, 6.4%).

*$\beta$ -m-Tolylethylmethylaniline.*—The carefully dried piperonal compound (15 g.) was mixed with an equal weight of methyl iodide and heated for 6 hours in a sealed tube at  $100^{\circ}$ . The excess of methyl iodide was boiled off and the residue dissolved in about 75 c.c. of 95% alcohol. On diluting the solution with three times its volume of ether, the *hydriodide* of the secondary base was precipitated in needles which, after being washed with ether, were faintly yellow and had m. p.  $107^{\circ}$  (Found : I, 45.5.  $C_{10}H_{15}N, HI$  requires I, 45.8%).

The free base, obtained by dissolving the hydriodide in an excess of 10% sodium hydroxide and extracting with ether, had b. p.  $88$ – $89^{\circ}/12$  mm. (Found : C, 80.5; H, 9.8; N, 9.6.  $C_{10}H_{15}N$  requires C, 80.5; H, 10.1; N, 9.4%).

The *hydrochloride* was best prepared by passing dry hydrogen chloride into a solution of the base in chloroform and adding ligroin, when it separated in greasy-looking leaflets, m. p.  $134^{\circ}$ . It is very soluble in alcohol and water and is usually obtained from these solvents, on evaporation, as an oil.

The *picrate* separated in orange needles, on mixing strong alcoholic solutions of the base and picric acid, and had m. p.  $126$ – $127^{\circ}$  (Found : N, 14.7.  $C_{10}H_{15}N, C_6H_3O_7N_3$  requires N, 14.8%).

The benzoyl derivative was obtained as a viscous oil on mixing the base with benzoyl chloride and dilute caustic soda. It showed no signs of crystallisation even on cooling in a freezing mixture.

*m-Methylstyrene.*—The quaternary methiodide of  $\beta$ -m-tolylethylamine (9 g.) was heated on the water-bath with 25% methyl-alcoholic potash (20 g.) in a small flask fitted with a reflux condenser closed with a cork, through which passed a delivery tube dipping into dilute hydrochloric acid. After 1 hour, when the decomposition appeared to be complete, water was added, the insoluble oily layer extracted with ether, and the ethereal solution washed with very dilute hydrochloric acid, dried, and distilled. The hydrocarbon obtained (3–4 g.) had b. p.  $61$ – $62^{\circ}/18$  mm. (Found : C, 91.3; H, 8.5.  $C_9H_{10}$  requires C, 91.5; H, 8.5%).

From the hydrochloric acid solution through which the gaseous products of the decomposition had been passed, trimethylamine hydrochloride, m. p.  $280^{\circ}$  (decomp.) (compare Wagner, *Z. Kryst. Min.*, 1906, 43, 167) was obtained. The chloroplatinate prepared therefrom formed brown scales, m. p.  $242-243^{\circ}$  (compare Willstätter, *Ber.*, 1895, 28, 3287), and the picrate formed golden-yellow prisms, m. p.  $216^{\circ}$ , from alcohol (compare Delépine, *Ann. Chim.*, 1896, 8, 452). Conclusive evidence was thus obtained that trimethylamine, and not dimethylamine, is eliminated during this decomposition.

From the density and the observed value of the refractive index ( $n_D^{20}$  1.54029), von Braun calculated the molecular refraction of his hydrocarbon, assuming, of course, the composition (II), and obtained the value  $[R_L]_D$  45.33, whilst that calculated for the composition  $C_{10}H_{10}$  was 42.11. He attributes this large exaltation of 3.2 units to the presence of the meta-ring structure. If, however, the molecular refraction is calculated from the same data, but assuming the composition  $C_9H_{10}$ , the value 41.15 is obtained, whilst that predicted theoretically (using Conrady's constants) is 39.70—giving an exaltation of only 1.4 units. This exaltation is of the order to be expected in a substance of the structure (IX) ( $EM_a$  for the isomeric  $\beta$ -methylstyrene is 1.01 units).

*$\alpha\beta$ -Dibromo- $\alpha$ -m-tolylethane.*—*m*-Methylstyrene (1.5 g.) dissolved in 10 c.c. of carbon disulphide was cooled in ice and gradually treated with a solution of 2.1 g. of bromine in 10 c.c. of carbon disulphide. After evaporation of the solvent, the crystalline residue was dissolved in a small volume of warm alcohol, from which it separated in well-formed, large prisms, m. p.  $47^{\circ}$  (compare Müller, *loc. cit.*) (Found: C, 39.2; H, 3.8; Br, 57.5. Calc., C, 38.8; H, 3.6; Br, 57.6%).

*Reduction of p-Phenylenediacetonitrile and p-Tolylacetonitrile.*—The reduction of these two substances was carried out in precisely the same manner as that of the meta-isomerides.

The same product, viz.,  $\beta$ -*p*-tolylethylamine, was obtained from both, as well as recognisable quantities of *p*-xylene.

The  $\beta$ -*p*-tolylethylamine, obtained in about 50% yield by reducing the dinitrile and in nearly 60% yield from the mononitrile, had b. p.  $94-95^{\circ}/13$  mm. (Found: C, 79.6; H, 9.7; N, 10.7.  $C_9H_{13}N$  requires C, 80.0; H, 9.6; N, 10.4%).

The hydrochloride, which is quite sparingly soluble in water and nearly insoluble in cold alcohol, crystallises in large plates, m. p.  $218^{\circ}$  (Found: C, 63.4; H, 8.25.  $C_9H_{13}N \cdot HCl$  requires C, 63.0; H, 8.2%). The picrate forms pale yellow needles, m. p.  $155^{\circ}$ , from alcohol (Found: N, 15.7.  $C_9H_{13}N \cdot C_6H_3O_7N_3$  requires N, 15.4%).

The *benzoyl* derivative is very readily soluble in most solvents, but can be crystallised from a small volume of alcohol in colourless prisms, m. p. 89° (Found: C, 80.5; H, 7.1.  $C_{16}H_{17}ON$  requires C, 80.3; H, 7.2%). The quaternary *methiodide* has m. p. 244° and is sparingly soluble in cold alcohol.

On treatment with an excess of an acid solution of sodium nitrite, the amine was converted into  $\beta$ -*p*-tolylethyl alcohol, which had b. p. 112°/12 mm., and when warmed with *p*-nitrobenzoyl chloride was converted into a solid ester, which separated from alcohol in small, colourless needles, m. p. 91° (Found: C, 67.0; H, 5.45.  $C_{16}H_{15}O_4N$  requires C, 67.3; H, 5.3%).

With piperonal, the amine formed a beautifully crystalline condensation product, m. p. 107°, only sparingly soluble even in hot alcohol (Found: C, 76.7; H, 6.55.  $C_{17}H_{17}O_2N$  requires C, 76.4; H, 6.4%).

$\beta$ -*p*-Tolylethylmethylamine.—The piperonal compound was heated in a sealed tube with an excess of methyl iodide in the manner previously described. The hydriodide of the secondary base, obtained on decomposition of the product with aqueous alcohol, had m. p. 149°. From this the free base was obtained, b. p. 96°/12 mm. (Found: C, 80.4; H, 10.25; N, 9.4.  $C_{10}H_{15}N$  requires C, 80.5; H, 10.1; N, 9.4%).

The hydrochloride is readily soluble in most solvents, but does not exhibit the extreme solubility of the meta-isomeride. It separates from cold alcohol in plates, m. p. 191°. The picrate forms deep orange prisms, m. p. 135°, from alcohol (Found: N, 14.7.  $C_{16}H_{18}O_7N_4$  requires N, 14.8%).

*p*-Methylstyrene.— $\beta$ -*p*-Tolylethylamine hydriodide is readily converted into the hydrocarbon by boiling with 25% methyl-alcoholic potash.

*p*-Methylstyrene has b. p. 59–60°/12 mm. and does not appear to undergo polymerisation as rapidly as the meta-isomeride (Found: C, 91.2; H, 8.7.  $C_9H_{10}$  requires C, 91.5; H, 8.5%).

Treated in carbon disulphide solution with the equivalent of two atoms of bromine, it is converted into  $\alpha\beta$ -dibromo- $\alpha$ -*p*-tolylethane, m. p. 46° (compare Klages and Keil, *loc. cit.*) (Found: Br, 57.15. Calc., Br, 57.6%).

My thanks are due to the Ramsay Memorial Trustees for a Fellowship during the tenure of which this work was carried out. I also wish to thank Professor W. H. Perkin for his interest and advice and Dr. R. D. Haworth for some valuable suggestions.

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LXVIII.—*The Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part II. Tellurium Dioxide.*

By EDMUND BRYDGES RUDEHALL PRIDEAUX and  
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THE action of hydrofluoric acid upon tellurium dioxide was studied by Metzner (*Ann. Chim. Phys.*, 1898, 15, 203). The oxide dissolved in the 43–55% acid. On cooling to about  $-50^{\circ}$ , crystals were obtained which contained 53% of hydrogen fluoride. The solutions crystallised on evaporation to small bulk, and successive crops corresponded best with the formulæ  $2\text{TeF}_4 \cdot 3\text{TeO}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{TeF}_4 \cdot \text{TeO}_2 \cdot 2\text{H}_2\text{O}$ , the analyses of the latter compound being the more concordant and agreeing better with the formula assigned. The mother-liquor from this preparation was treated with hydrofluoric acid "pur." (from potassium hydrogen fluoride) and cooled to  $-70^{\circ}$ . It then formed transparent crystals containing 3.8 atoms of fluorine for each atom of tellurium. This compound was regarded as  $\text{TeF}_4$ . The author remarks that its preparation in the pure state would require very concentrated acid. We have used anhydrous hydrogen fluoride throughout our investigation, but have not so far observed the crystallisation of this compound. We have, however, confined our experiments mainly to the preparation of that fluoride which is obtained at the ordinary temperature.

EXPERIMENTAL.

Tellurium, supplied by the courtesy of the Baltimore Copper Company, was dissolved in nitric acid, and the solution evaporated to dryness. The product was slightly green owing to the presence of copper, which was removed by fusion with sodium carbonate and extraction with water followed by filtration. The solution was made faintly acid with nitric acid, and the precipitated tellurous acid was filtered off, dried at  $100^{\circ}$ , heated to its melting point, and powdered.

The anhydrous hydrogen fluoride, prepared as already described (Part I, this vol., p. 167), was passed over the dioxide in a platinum boat or crucible, contained in a copper tube or copper-plated cylinder, respectively. A colourless liquid was produced and a white solid, consisting apparently of unchanged tellurium dioxide, remained. This dissolved completely in excess of hydrogen fluoride. The liquid was exposed for several days in a vacuum desiccator, covered inside with ceresin and containing calcium chloride and solid sodium hydroxide. It became slightly more viscous and remained clear.

On cooling to  $-70^{\circ}$ , it became very viscous, but no crystals appeared on stirring and rubbing. After standing for another day, it suddenly set to a mass of white crystals. This is the product A mentioned below.

The preparation was repeated with slight variations. The hydrogen fluoride vapour was passed until some of the oxide had dissolved and some had been converted into silky crystals, which adhered firmly to the crucible. The liquid was then decanted into a platinum capsule. The undissolved dioxide and the silky crystals were dissolved in more liquid hydrogen fluoride which had been condensed in a platinum bottle. Both solutions were placed at once in the desiccator described above, which was then evacuated. After about 2 days, a mass of white nodules of radiating crystalline structure separated from each solution. This is sample B.

These crystals were kept, in a desiccator, unchanged for days at atmospheric pressure. When the desiccator was evacuated over phosphorus pentoxide for a night, 0.5525 g. of the substance lost only 3 mg. But when this treatment was continued for several days (sample B1) or when the compound was kept over alkali in a desiccator for months (sample A1), the composition changed in the manner indicated by the analyses given below.

*Analysis.*—Since the accurate gravimetric estimation of fluoride in the presence of tellurite is difficult (Metzner, *loc. cit.*), we have devised a method of estimating it as hydrogen fluoride after hydrolysis. When a solution of tellurous acid in dilute hydrofluoric acid is titrated with alkali in the presence of *p*-nitrophenol, precipitation of tellurous acid begins at once and continues until the indicator turns yellow. When tellurous acid is suspended in water, a single drop of alkali produces this colour change. Therefore, on account of its sparing solubility, the tellurous acid gives a solution of  $[H^{+}] = 1 \times 10^{-5}$  or even less. A weighed amount of hydrofluoric acid, when titrated in the presence of tellurous acid, required exactly the same amount of alkali as the same weight of hydrofluoric acid when titrated alone. Tellurous acid, therefore, can be disregarded at the *p*-nitrophenol end-point. Although this titration gives concordant figures, these do not, as shown in Part I (*loc. cit.*), correspond with the absolute amount of hydrofluoric acid present until multiplied by a factor 1.03.

The samples were analysed after being crushed and rubbed between filter-paper.

Tellurium was estimated as usual after precipitation by sulphur dioxide from a hydrochloric acid solution.\*

\* In the volumetric analysis, the titrated liquid was proved to be free from tellurium, and the precipitate free from fluoride.

Sample A : 0.273 g. required 28.57 c.c. of *N*/10-alkali and gave 0.1805 g. of tellurium. Sample B : 0.9005 g. required 92.3 c.c. of *N*/10-alkali, and 0.382 g. gave 0.2545 g. of tellurium.

	A.	B.	A1.	B1.
% Te	66.1	66.6	68.7	70.2
% F	20.4	20.0	18.6	18.9

$\text{TeF}_4 \cdot \text{TeO}_2 \cdot \text{H}_2\text{O}$  requires Te, 66.8; F, 20.0%.  $\text{TeF}_4 \cdot \text{TeO}_2 \cdot 2\text{H}_2\text{O}$  requires Te, 63.8; F, 19.1%.

The use of anhydrous hydrogen fluoride therefore leads to a compound different from either of those prepared by Metzner. In the presence of more water, more hydrated compounds would doubtless be formed. Since the only water present in our experiments was that formed in the reaction, it is evident that at least one molecule is thus produced and evaporates in the desiccator. The other molecule, if it is really eliminated, is held as water of crystallisation but has only a low vapour pressure.

We regard this compound as the least hydrated which it is possible to prepare from the dioxide and hydrogen fluoride with subsequent evaporation. It is not at present possible to decide between the formulæ  $\text{TeF}_4 \cdot \text{TeO}_2 \cdot \text{H}_2\text{O}$ ,  $2\text{TeOF}_2 \cdot \text{H}_2\text{O}$ , and  $\text{TeOF}_2 \cdot \text{TeO}_2 \cdot 2\text{HF}$ . In material kept in the desiccator after a long time (A1), or in a vacuum over phosphorus pentoxide (B1), the percentage of tellurium increases considerably, whilst the percentage of fluorine diminishes only slightly. These results suggest that, under the conditions employed, more water is lost than hydrogen fluoride, so that the compound behaves rather as a hydrate than as a fluoride.

One of us wishes to repeat his grateful acknowledgment to the Royal Society of a grant which has supplied some of the apparatus required for this and the preceding research. The other (J. O'N. M.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant.

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## LXIX.—*The Action of Alcoholic Potassium Hydroxide upon Chloronitrobenzene.*

By DONALD HENRY RICHARDSON.

LEUMANN (*Ber.*, 1872, 5, 910) obtained *pp'*-dichloroazoxybenzene by boiling *p*-chloronitrobenzene with alcoholic potash. Willgerodt (*Ber.*, 1879, 12, 767) showed that *p*-nitrophenetole and *p*-nitrophenol also are products of the reaction, and later (*Ber.*, 1882, 15, 1002) found that dilution of the alcohol with water diminishes the form-



ation of dichloroazoxybenzene. Blom (*Helv. Chim. Acta*, 1921, 4, 297) studied the kinetics of the reaction and found that by using aqueous alcohol at 70° no dichloroazoxybenzene is formed.

In an investigation with the object of discovering the conditions under which the maximum yield of nitrophenetole free from chloronitrobenzene could be most easily obtained, it was found that the formation of dichloroazoxybenzene could be avoided without dilution of the alcohol if the temperature was reduced to 60°, and the alkali strength to 0.2 normal. Excellent results having been obtained on the small scale, some large-scale trials were made in which 362 lb. of chloronitrobenzene were heated at 60° with 145 gallons of 0.2*N*-95% alcoholic soda, the alkali strength being maintained by the addition of the estimated amount of the powdered solid at frequent intervals. At the first attempt, in spite of considerable accidental loss, the yield amounted to 277 lb. of nitrophenetole, free from chloronitrobenzene, and containing only 3.4% of dichloroazoxybenzene, but in all subsequent experiments at least 17% of the theoretical amount of azoxy-compound was formed. It was not realised at the time that the alcohol used in the first experiment had been specially purified for pharmaceutical purposes, and the systematic investigation to be described was undertaken to discover the cause of the failure of the process.

The conclusions are as follows :

1. The presence of as much as 0.1% of acetaldehyde in the alcohol causes considerable reduction of the chloronitrobenzene, and the larger the percentage of acetaldehyde, the greater is the yield of dichloroazoxybenzene.

2. The formation of dichloroazoxybenzene may be avoided without dilution of the alcohol with water if chloronitrobenzene is heated for 140 hours at 60° in a 0.5*N*-solution of caustic potash in 95% ethyl alcohol free from acetaldehyde.

3. Under these conditions, 92% of the theoretical yield of pure *p*-nitrophenetole, 90% of *o*-nitrophenetole, and 96% of *p*-nitroanisole (using methyl alcohol) may be obtained, nitrophenol being the only by-product.

4. As the temperature or alkali concentration is raised, dichloroazoxybenzene is formed in rapidly increasing amount, even if the alcohol is free from acetaldehyde.

5. Under conditions resulting in the formation of a considerable amount of dichloroazoxybenzene, *p*-chloroaniline is also formed in appreciable quantity.

6. Although the reducing action of alcoholic alkali is decreased by dilution of the alcohol with water (Willgerodt, *loc. cit.*), this diminishes the rate of conversion of chloronitrobenzene into nitrophenetole.

7. Nitrophenol is always a by-product when chloronitrobenzene is heated with alcoholic alkali solution, and the yield is increased as the temperature and the strength of alkali are raised, but is not greatly affected by dilution of the alcohol with water.

### EXPERIMENTAL.

Five series of experiments were carried out, in each of which only one factor was subjected to variation. Pure chloronitrobenzene was heated at a constant temperature in a large excess of a standard solution of potash in alcohol of known strength. After a noted time, the solution was nearly neutralised with sulphuric acid, the alcohol distilled off, and the nitrophenetole isolated by blowing steam through the residue. Its weight and melting point were determined after filtering off and drying over calcium chloride in a vacuum desiccator. Nitrophenetole was appreciably volatile in alcohol vapour, and was estimated in the alcohol recovered by evaporating a known volume in a vacuum desiccator at laboratory temperature, and weighing the residue. Ether extraction of the filtered steam distillate showed that nitrophenetole was soluble in water at 15° to the extent of 0.11 g. per litre. The insoluble dichloroazoxybenzene was filtered off from the residual liquors, washed, dried, and weighed without further purification. After evaporation to smaller bulk, the filtrate and washings were acidified with sulphuric acid and the *p*-nitrophenol was extracted with ether.

The conditions in each series of experiments are described below, and the yields given in tabular form.

*Series 1.—Variation in strength of alkali.* A solution of caustic potash in 95% alcohol was standardised and diluted with the calculated volume of alcohol so that 250 c.c. each of a 0.1, 0.2, 0.3, 0.4, and 0.5 *N*-solution of potash were obtained. Exactly 4 g. of pure chloronitrobenzene were dissolved in each solution, and all were heated together in a thermostat at 60°. After 187 hours' heating, 5 c.c. of each solution were titrated with *N*/10-sulphuric acid to determine the final concentration of the potash, and the reaction products analysed as previously described. The results are tabulated below:

Experiment.	1.	2.	3.	4.	5.
Strength of KOH ( <i>N</i> ): initial ...	0.1	0.2	0.3	0.4	0.5
final ...	0.013	0.064	0.165	0.226	0.405
Wt. of nitrophenetole (g.) .....	3.19	3.61	3.24	2.86	1.91
M. p. of nitrophenetole .....	46°	57°	57°	57°	57°
Wt. of dichloroazoxybenzene (g.) ..	0.02	0.10	0.37	0.70	0.92
Wt. of <i>p</i> -nitrophenol (g.) .....	0.04	0.09	0.13	0.28	0.50
% Theoretical yield:					
Nitrophenetole .....	75.3	85.1	76.4	67.5	44.8
Dichloroazoxybenzene .....	0.6	2.9	10.9	20.6	27.1
Nitrophenol .....	1.1	2.6	3.7	7.9	14.2
Total .....	77.0	90.6	91.0	96.0	86.1

The low melting point of the nitrophenetole obtained in experiment 1 showed that some unchanged chloronitrobenzene remained, as would be expected in view of the small final concentration of the potash in this case. A considerable amount of tarry matter was noted during the extraction of the nitrophenol in experiment 5, and a smaller amount in experiment 4. It was not found possible to account for the remainder of the yield at this point.

The results indicated that an increase in the concentration of alkali causes a greater production of both dichloroazoxybenzene and nitrophenol, this being most marked in the case of the azoxy-compound.

*Series 2.—Variation in strength of alcohol.* Five 0.5*N*-potash solutions were prepared, one in absolute alcohol, and the other four in 95% alcohol diluted with noted volumes of water to a total of 250 c.c. each. The five solutions were heated in a constant-temperature water-bath at 60° for 24 hours, after which 4 g. of chloronitrobenzene were dissolved in each and the heating was continued for 187 hours.

The products were analysed with the following results :

Experiment.	6.	7.	8.	9.	10.
Strength of alcohol (%) .....	100	87	80	70	60
Wt. of nitrophenetole (g.) .....	3.834	3.497	3.453	3.348	3.019
M. p. of nitrophenetole .....	57°	57°	57°	56°	56°
Wt. of dichloroazoxybenzene (g.)	0.025	0.129	0.157	0.071	0.106
Wt. of nitrophenol (g.) .....	Lost by accident.	0.484	0.488	0.469	0.455
% Theoretical yield :					
Nitrophenetole.....	90.4	82.5	81.4	78.9	71.2
Dichloroazoxybenzene .....	0.7	3.8	4.6	2.1	3.1
Nitrophenol .....	?	13.7	13.8	13.3	12.9
Total .....	(91.1)	100.0	99.8	94.3	87.2

The melting point of the nitrophenetole obtained in experiments 9 and 10 showed that a small amount of chloronitrobenzene remained unchanged, indicating that dilution of the alcohol retards the rate of conversion of chloronitrobenzene into nitrophenetole. The most remarkable result was the very small yield of dichloroazoxybenzene in all five experiments, in spite of a concentration of potash equal to that in experiment 5, in which a 27% yield of the azoxy-compound was obtained.

The use of absolute alcohol having resulted in the smallest production of dichloroazoxybenzene, it seemed probable that some impurity in the alcohol was the cause of the formation of the azoxy-compound. Since the chloronitrobenzene is reduced to dichloroazoxybenzene, acetaldehyde would be the most likely impurity to cause this reduction. The preliminary 24 hours' heating of the alcoholic potash before the introduction of the chloronitrobenzene would have at least partly resinified the aldehyde, so accounting

for the small yield of dichloroazoxybenzene in these five experiments. It was noted that a yellow colour developed in the alcoholic potash solutions during the preliminary heating, indicating the formation of aldehyde-resin.

*Series 3.—Effect of acetaldehyde upon the production of dichloroazoxybenzene.* To determine the effect of acetaldehyde upon chloronitrobenzene in alcoholic potash solution, a third series of five experiments was commenced, using 250 c.c. of 0.5 *N*-alkali in 95% alcohol. The chloronitrobenzene was added before heating in experiment 11, but after 66 hours' preliminary heating in experiment 12, while 25 c.c. of hydrogen peroxide solution were added in experiment 13. Methylated spirit known to contain acetaldehyde was used in experiment 14, and 10 c.c. of acetaldehyde were added to the alcohol in experiment 15, in both cases the chloronitrobenzene being added before heating was commenced. The five solutions were heated simultaneously for 235 hours at 60°, and gave the following yields on analysis:

Experiment.	11.	12.	13.	14.	15.
Wt. of nitrophenetole (g.) .....	3.69	3.77	3.58	2.13	0.82
Wt. of dichloroazoxybenzene (g.) .....	0.04	0.02	0.015	0.315	2.29*
Wt. of nitrophenol (g.) .....	0.43	0.41	0.52	0.68†	0.67†
% Theoretical yield:					
Nitrophenetole.....	87.0	88.9	84.4	50.2	19.2
Dichloroazoxybenzene .....	1.2	0.6	0.5	9.3	67.6*
Nitrophenol .....	12.2	11.5	14.7	19.5†	19.0†
Total .....	100.4	101.0	99.6	79.0	105.8.

\* Includes aldehyde-resin.

† Includes tar.

The very large yield of dichloroazoxybenzene in the presence of acetaldehyde left little cause for doubt that the latter plays an important part in the reduction of the chloronitrobenzene. It was resolved to test this conclusion by heating chloronitrobenzene with alcoholic potash containing known small quantities of acetaldehyde.

Acetaldehyde was eliminated from ethyl alcohol as completely as possible by refluxing with 0.2% of *m*-phenylenediamine hydrochloride for 12 hours, after which the alcohol was distilled off through a fractionating column, the first 100 c.c. of the distillate being rejected. The product gave no colour on standing with Schiff's reagent, and remained practically colourless after heating for 24 hours with 0.5*N*-potash at 60°.

A standard solution of acetaldehyde was prepared by dissolving about 10 c.c. of freshly distilled acetaldehyde (b. p. 21°) in 100 c.c. of aldehyde-free alcohol and estimating its strength by the sodium sulphite method.

*Series 4.—Effect of variation in concentration of aldehyde.* Three solutions were prepared containing measured volumes of the standard acetaldehyde solution diluted to 250 c.c. with aldehyde-free

alcohol in which was dissolved sufficient potash to give 250 c.c. of a 0.5*N*-solution. Four g. of chloronitrobenzene were dissolved in each, and all were heated simultaneously with a blank experiment, using the same aldehyde-free alcohol, for 160 hours at 60°. The following table gives the yields in the four experiments :

Experiment.	16.	17.	18.	19.
Strength of acetaldehyde (%) .....	0.0	0.14	0.2	0.67
Wt. of nitrophenetole (g.) .....	3.902	3.434	2.685	1.121
Wt. of dichloroazoxybenzene (g.) ...	Nil	0.317	0.536	2.178†
Wt. of nitrophenol (g.) .....	0.276	0.210	0.405*	0.463*
% Theoretical yield :				
Nitrophenetole .....	92.0	81.0	63.3	26.4
Dichloroazoxybenzene .....	0.0	9.3	15.8	64.2†
Nitrophenol .....	7.8	5.9	11.5*	13.3*
Total .....	99.8	96.2	90.6	103.9

\* Includes tar.

† Contained aldehyde-resin.

From these results, it is evident that the complete elimination of acetaldehyde from the reaction mixture prevents the formation of dichloroazoxybenzene, under the conditions obtaining in these experiments. As little as 0.1% of acetaldehyde appears to be capable of causing a considerable amount of reduction of the chloronitrobenzene, and an increase in the concentration of the aldehyde, within the limits investigated, causes a corresponding increase in the formation of dichloroazoxybenzene.

Experiments were now made to determine whether, with the use of aldehyde-free alcohol, the temperature and the alkali concentration could be increased without the formation of dichloroazoxybenzene. It had been noted that whenever the latter appeared in the reaction product in any quantity, the total yields of nitrophenetole, dichloroazoxybenzene, and nitrophenol did not account for the whole of the chloronitrobenzene employed. It was thought possible that a small amount of the latter might have become completely reduced to *p*-chloroaniline.

To investigate this possibility, the solutions obtained in the following series of experiments were acidified with dilute sulphuric acid before distilling off the alcohol. After steam distillation of the nitrophenetole and filtration of the dichloroazoxybenzene, the acid filtrate was made alkaline and distilled to a small volume. The distillate was extracted with ether, and the residue after its evaporation weighed.

The residue melted at 66°, was soluble in dilute acids and reprecipitated by alkali, and could be diazotised and coupled with  $\beta$ -naphthol to give a red dye. It was acetylated with acetyl chloride, and the product melted at 171–173°. After recrystallisation from dilute alcohol, it melted sharply at 177°. These facts indicated that the residue was *p*-chloroaniline.

*Series 5.—Effect of higher temperature, and greater concentration of alkali, on the reaction of chloronitrobenzene with aldehyde-free alcoholic potash.* Five solutions of potash in 250 c.c. of aldehyde-free alcohol were prepared so that two contained 0.5*N*-alkali, and the other three 1.0, 1.5, and 2.0 *N*-alkali, respectively. In each were dissolved 4 g. of chloronitrobenzene, and, whilst one of the 0.5 *N*-solutions was refluxed for 24 hours, the other four were heated for 140 hours at 60°.

The yields of nitrophenetole, nitrophenol, dichloroazoxybenzene, and chloroaniline in each of the five experiments were estimated as described above, with the following results :

Experiment.	20.	21.	22.	23.	24.
Strength of potash ( <i>N</i> ) .....	0.5	0.5	1.0	1.5	2.0
Wt. of nitrophenetole (g.) .....	1.241	3.800	2.134	0.778	0.328
Wt. of nitrophenol (g.) .....	0.553	0.279	0.434	0.364	0.304
Wt. of dichloroazoxybenzene (g.) .....	1.526	Nil	0.988	2.243	2.372
Wt. of <i>p</i> -chloroaniline (g.) .....	0.205	Nil	0.338	0.293	0.572
% Theoretical yield :					
Nitrophenetole.....	29.3	89.6	50.3	18.4	7.7
Dichloroazoxybenzene .....	45.0	0.0	29.1	66.2	70.0
Chloroaniline .....	6.3	0.0	10.4	9.1	17.7
Nitrophenol .....	15.7	7.9	12.3	10.3	8.6
Total .....	96.3	97.5	102.1	104.0	104.0

Refluxed.

The dichloroazoxybenzene  
was very impure.

These results proved conclusively that the absence of aldehyde from the alcohol does not preclude the formation of dichloroazoxybenzene under all conditions. They confirm the conclusion that higher temperature and higher concentration of alkali favour the reduction of the chloronitrobenzene, an appreciable quantity of which becomes completely reduced to *p*-chloroaniline whenever dichloroazoxybenzene is formed to any extent.

In order to determine the minimum time required for the conversion of chloronitrobenzene into nitrophenetole under the conditions giving the maximum yield, 63 g. of chloronitrobenzene in 2 litres of 0.5*N*-95% aldehyde-free alcoholic potash were heated at 60°, whilst 5 c.c. of the solution were titrated at intervals with *N*/10-acid, and the melting point of the precipitated chloronitrobenzene-nitrophenetole mixture was determined.

#### Experiment 25.

Time (hours).	<i>N</i> /10- $\text{H}_2\text{SO}_4$ (c.c.) for 5 c.c.	Strength of KOH ( <i>N</i> ).	Equivs. of KOH M. neutralised.	p. of pptd. product.
0	25	0.5	0.0	83°
28½	18.45	0.369	0.655	49—51
50	16.85	0.337	0.815	54—55
78½	15.75	0.315	0.925	55—56
142	15.0	0.300	1.0	56—57

After 142 hours, the whole solution was neutralised with dilute sulphuric acid, and the alcohol distilled off on the water-bath. The residue of nitrophenetole was well washed with dilute caustic soda to remove nitrophenol, then with water, and dried over calcium chloride in a vacuum desiccator. The mother-liquors and washings were evaporated down, acidified, and extracted with ether.

Yield :	61.1 g. of nitrophenetole, m. p. 56.5°	= 91.5% of theor.
	3.3 g. of nitrophenol	= 6.0 " "
	20 c.c. of solution withdrawn for titration	= 1.0 " "
	Total	= 98.5 " "

This experiment confirmed the conclusion that *p*-chloronitrobenzene can be converted into nitrophenetole by heating at 60° for approximately 140 hours in 0.5 *N*-95% alcoholic potash, without the formation of any dichloroazoxybenzene, if the alcohol is free from acetaldehyde.

Under similar conditions, 65 g. of *o*-chloronitrobenzene, dissolved in 1 litre of aldehyde-free ethyl alcohol, gave a yield of 62.2 g. of *o*-nitrophenetole (90.3% of the theoretical), whilst 4 g. of *p*-chloronitrobenzene in 250 c.c. of methyl alcohol gave 3.750 g. of *p*-nitroanisole (96.5% of the theoretical).

No dichloroazoxybenzene was formed in either case.

NORTHERN POLYTECHNIC, LONDON, N.7. [Received, October 30th, 1925.]

## LXX.—Action of Mercurous Nitrate on Chloroauric Acid.

By WILLIAM BRANCH POLLARD.

THE action of mercurous nitrate on chloroauric acid has been stated to give (1) gold, or a mixture of gold and mercurous chloride (Proust, *Nicholson's J.*, 1806, **13**, 244); (2) a combination of aurous and mercuric oxides (Fischer, *Schweigger's J.*, 1829, **56**, 363), (3) aurous oxide (Figuier, *Ann. Chim. Phys.*, 1844, **11**, 336).

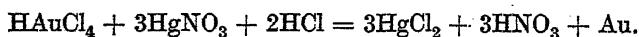
The author has studied the reaction under two distinct conditions; first, the reaction which occurs when an excess of some halide is present, and, secondly, the reaction which occurs in the absence of halides.

### EXPERIMENTAL.

*Action of Mercurous Nitrate on Chloroauric Acid in Presence of Halides.*—Mercurous nitrate was prepared by shaking a solution of mercuric nitrate in dilute nitric acid with excess of mercury, a little carbamide being added to prevent the formation of nitrites. The solution was titrated as described below, and then diluted until 50 c.c. reduced exactly 0.5 g. of gold.

Gold (0.5 g.) was dissolved in 4 c.c. of aqua regia (3 : 1). The fumes were blown out with a current of air, but the excess of nitric and hydrochloric acids was not removed. The solution was diluted with 50 c.c. of water, 1 c.c. of concentrated hydrochloric acid was added, and mercurous nitrate solution run in. The black colour of the precipitate of metallic gold that instantly formed slowly changed to brown. The particles of the precipitate cohered on shaking, leaving the liquid clear. As the end-point was approached, the yellow colour of the chlorauric acid disappeared, the precipitate took on a transient purple tint, and finally white, mercurous chloride formed. During the titration, no evidence of reduction to the aurous state was obtained, even when a large amount of alkali-metal chloride was present (Diemer, *J. Amer. Chem. Soc.*, 1913, **35**, 552). Addition of such chlorides or of bromides or iodides appears to increase the velocity of the reaction. The amount of mercurous nitrate required to precipitate the gold when in combination with chlorine, bromine, or iodine was, however, practically identical in the three cases, provided there was sufficient halide to combine with the whole of the mercury present.

In order to obtain the quantitative relation between mercurous nitrate and chlorauric acid, the volume of solution required to precipitate 0.5 g. of pure gold was taken and precipitated with sodium chloride. The resulting mercurous chloride was equivalent to 2.0039 g. of mercurous nitrate as against 1.9947 g. required by the equation :



To test whether this relation held at very great dilutions, the mercurous nitrate and chlorauric acid were titrated at a dilution one hundred times as great as that employed above. The gold separated in the red, colloidal condition. It was flocculated with a little hydrochloric acid, and the end-point found by addition of o-tolidine (*Trans. Inst. Min. Met.*, 1923, **32**, 242), which gives a yellow colour with one part of chlorauric acid in twenty million parts of solution. At this dilution, the relationship found above still held.

From this experiment it is inferred that the precipitate which forms when strong solutions react consists of colloidal gold which has been flocculated by the acids and salts present in the liquid, and this would also account for the very marked adsorption effects which have been observed.

When 0.5 g. of the precipitated gold was shaken with a solution containing a few mg. of chlorauric acid, this substance was so completely adsorbed that it could not be detected in the solution.



The adsorbed substance reacted quite readily with solutions of reducing agents when these were applied to the precipitate.

When solutions of certain dyes were shaken with the precipitate, these became colourless, and in the case of methyl-red this was adsorbed more readily in an acid than in an alkaline solution.

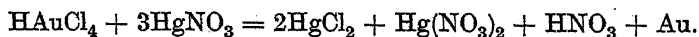
In the course of these experiments it was noticed that if a very small amount of brucine or one of the quinine alkaloids was added to the chloroauric acid before precipitation with mercurous nitrate, the gold remained dispersed through the liquid and did not flocculate. Up to the present this result has not been observed except with the class of substances mentioned.

*Action of Mercurous Nitrate on Chloroauric Acid in the Absence of Halides.*—Gold (0.5 g.) was converted into chloroauric acid, and all excess of nitric and hydrochloric acids was removed; 50 c.c. of water were added and mercurous nitrate solution was run in. The precipitate did not "clear" on shaking and the end-point was difficult to find, but much less mercurous nitrate was needed to precipitate the gold completely in the absence of halides than in their presence.

To a fresh solution of chloroauric acid a little mercurous nitrate was added, in order to precipitate only a small part of the gold. The black precipitate, on standing over-night in the solution, was converted into metallic gold. The gold was separated from the solution, and a further amount of mercurous nitrate added. The black, colloidal precipitate which formed was centrifuged, and the clear solution, which had changed from yellow to reddish-brown, was further examined. When heated, a reddish-brown precipitate resembling ferric hydroxide formed, and the same substance was deposited when the solution was kept.

The substance was difficult to filter and wash, and after drying in a vacuum over sulphuric acid gained weight when exposed to the air. When heated, it gave off oxygen, water, and mercuric chloride, and left a residue of metallic gold. It dissolved in hydrochloric acid with the reformation of chloroauric acid.

If the equation for the reaction between mercurous nitrate and chloroauric acid is written omitting the hydrochloric acid from the left-hand side, this will require the addition of mercuric nitrate to the right-hand side:



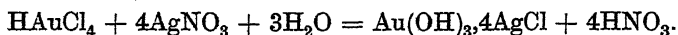
Now Proust (*loc. cit.*, p. 224) showed that when "gold chloride" was added to an excess of mercuric nitrate solution a yellow precipitate formed. This compound gave oxygen, water, mercuric chloride, mercurous chloride, and gold on heating. The brown

compound prepared by the author gave no mercurous chloride when heated.

On adding a small amount of mercuric nitrate to chloroauric acid, a slight darkening of the solution occurred. Further additions produced a reddish-brown solution similar to that previously obtained after centrifuging. When heated, a brown, colloidal precipitate separated identical with that previously described. The brown substance is therefore formed when chloroauric acid is in excess and Proust's yellow substance is formed when mercuric nitrate is in excess.

Proust explained the formation of his compound as being due to the very strong affinity of mercury for chlorine, which it is able to displace even from chloroauric acid.

Jacobson (*Compt. rend.*, 1908, **146**, 1213) has shown that silver nitrate also can remove chlorine from chloroauric acid with formation of a brown basic compound :



Attempts to discover the exact composition of the brown substance failed, as different preparations did not show sufficient agreement among themselves, and it is doubtful whether it has been prepared as yet in a state of purity. The following results, obtained by heating the substance in a Penfield tube, may, however, be taken as an approximate indication of its nature: Loss on heating (oxygen), 9.42;  $\text{H}_2\text{O}$ , 7.18;  $\text{HgCl}_2$ , 19.71; Gold (by difference), 63.69%.

The black precipitate formed by the action of mercurous nitrate on chloroauric acid which had been centrifuged out of the solution was now examined to see whether it consisted of a mixture of gold and the brown substance. After washing and drying, it was heated and gave off oxygen, water, and mercuric chloride and left a residue of gold. When it was treated with hydrochloric acid, chloroauric acid passed into solution and a residue of metallic gold was left. The black precipitate may therefore be regarded as a kind of "Purple of Cassius" in which stannic acid is replaced by the brown substance. It results from two reactions occurring simultaneously, which explains why, in the absence of halides, less mercurous nitrate is required to remove the gold completely from solution.

The author takes this opportunity of thanking Professor Carpenter and the staff of the Royal School of Mines for all the facilities which he has been afforded.

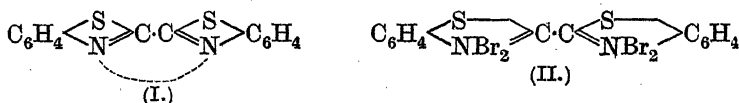
ROYAL SCHOOL OF MINES,  
SOUTH KENSINGTON.

[Received, October 17th, 1925.]

LXXI.—*Halogenation of 2:6-Dimethylbenzbisthiazole and of 3:5-Diphenylimino-2:4-diphenyltetrahydro-1:2:4-thiodiazole.*

By ROBERT FERGUS HUNTER.

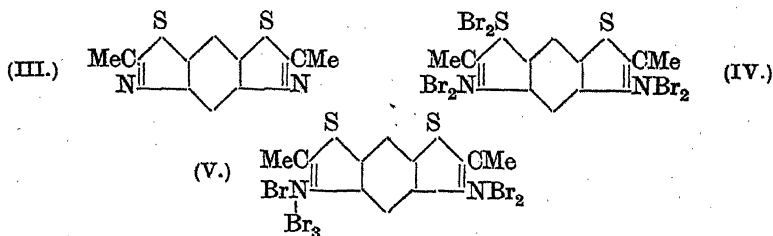
THE slight unsaturation of the nitrogen atoms of the heterocyclic nuclei in 1:1-bisbenzthiazole (I) and the consequent great lability of the tetrabromide (II), which is so unstable that it decomposes appreciably into the original bisthiazole (I) and bromine on exposure to air for a few minutes (J., 1925, 127, 1319), must, in view of the stability of 1-substituted benzthiazole bromides such as 1-phenylbenzthiazole tetrabromide (*loc. cit.*), clearly be due to the presence of the second thiazole nucleus.



That is to say that the two thiazole nuclei joined as in (I) by way of their  $\mu$ -carbon atoms, mutually "saturate" each other.

Regarding this effect, it seems reasonable to suggest that the phenomenon is due to partial self-neutralisation of the valencies of the nitrogen atoms after the manner in which the central pairs of partial valencies in conjugated systems neutralise each other according to Thiele's theory (*Annalen*, 1899, 306, 87). This supposition can be represented by means of a dotted line as in (I).

In view of this, it was clearly desirable to examine the unsaturation of the benzbisthiazole system in which the thiazole nuclei are separated from each other by a benzene ring which should inhibit or prevent the self-saturation effect displayed by 1:1-bisbenzthiazole. The example chosen was 2:6-dimethylbenzbisthiazole (III) (Edge, J., 1922, 121, 772).



The reactive nitrogen atoms in this case are not linked by way of the  $\cdot\text{N}:\text{C}:\text{C}:\text{N}\cdot$  system, but this is immaterial, since the supposed double bonds in the thiazole nucleus are aromatic in character, and the usual formula for the thiazole ring really can represent only one

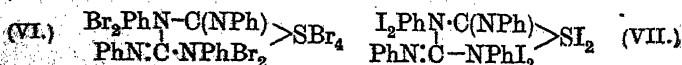
of the transient phases of the intra-annular semi-aromatic heterocyclic nucleus.

2 : 6-Dimethylbenzbisthiazole in presence of excess of bromine readily passes into a bright yellowish-orange, relatively stable *hexabromide*, the most probable constitution of which is (IV). This bromo-additive compound is quite devoid of the properties of 1 : 1-bisbenzthiazole tetrabromide; for instance, it only loses appreciable halogen on exposure to the atmosphere for several days and is in many ways similar to the stable tribromo-additive compounds of the arylaminobenzthiazoles (J., 1925, 127, 2024). The self-saturation effect of the thiazole nuclei is therefore removed by the intervention of the common aromatic nucleus. There is, however, another effect which arises in connexion with the unsaturation of the benzbisthiazole complex, namely, the alternation of the affinity effect of carbon chains (Flürscheim, *J. pr. Chem.*, 1902, 66, 321; J., 1909, 95, 718; 1910, 97, 84; Ingold, J., 1925, 127, 513), which operates in the manner described hereunder.

In the bromination of 2 : 6-dimethylbenzbisthiazole, the first reaction must necessarily consist in the addition of bromine to *one* of the ring nitrogen atoms. The consequent formation of the  $\text{:NBr}_2$  group at once causes an alternation in affinity along the carbon chain connected to the second nitrogen atom, which therefore becomes partly saturated. Now there can be very little doubt, from the facts already described in connexion with the bromo-additive compounds of the benzthiazoles (*loc. cit.*), that the *centre* of unsaturation in a thiazole ring is the *nitrogen* atom. The obvious result is that in the bromination of the benzbisthiazole system one thiazole nucleus is much more *reactive* than the other, and hence one ring is responsible for the addition of four bromine atoms, whilst the other is fully satisfied by the addition of two. In this connexion, it does not matter whether the hexabromide has the constitution (IV) or the less probable formula (V).

The above is well borne out by the behaviour of 2 : 6-dimethylbenzbisthiazole towards other reagents such as methyl iodide; even in the presence of a large excess of methyl iodide, it will form only a monomethiodide (Edge, *loc. cit.*).

Since benzbisthiazole is in a sense a dithio-di-azo-heterocyclic compound, it was of interest to examine the thiodiazole complex. The example chosen was 3 : 5-diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole (Hector, *Ber.*, 1890, 23, 357), which would be expected to pass under suitable conditions into the octabromide (VI).



Actually an *octabromide* having the expected properties was readily isolated as a bright red, crystalline compound, which gradually lost bromine on exposure to the atmosphere and was reduced by sulphurous acid (Hunter, *loc. cit.*) with regeneration of the original thiodiazole.

There are, however, alternative formulæ for this compound involving the  $\text{Br}\cdot\text{N}\cdot\text{Br}$   $\begin{smallmatrix} \text{Br} \\ | \\ \text{N} \\ | \\ \text{Br} \end{smallmatrix}$  group. In view of the lesser affinity of iodine as compared with bromine for sulphur (compare Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, **44**, 826) and the facility iodine atoms have for combining with one another, which is greater even than that of bromine atoms, if the octabromide is indeed (VI), it might be expected that the thiodiazole on treatment with iodine would yield an additive compound of a *lower* order; whilst if the existence of the octabromide were due to the presence of the  $\text{Br}\cdot\text{N}\cdot\text{Br}$  group, an octaiodide would be formed. Actually the only iodo-additive compound isolated was a *hexaiodide*, which is best represented by the formula (VII). Its formation is by no means a crucial test, but is in favour of the formulæ suggested for these additive compounds.

#### EXPERIMENTAL.

Dithioacetyl-*m*-phenylenediamine was prepared from diacetyl-*m*-phenylenediamine (20 g.) and oxidised with potassium ferricyanide according to Edge's directions (*loc. cit.*). The product isolated from the ethereal extract was allowed to crystallise spontaneously from light petroleum-alcohol and recrystallised (without distillation) from light petroleum, 2 : 6-dimethylbenzbisthiazole being thus obtained in shining prisms, *m. p.* 105°.

2 : 6-Dimethylbenzbisthiazole *Hexabromide*.—The benzbisthiazole (0.25 g.) dissolved in chloroform (5 c.c.) was slowly treated with bromine (0.3 c.c.). The solution was then either warmed and rapidly treated with a further quantity of bromine (0.3 c.c.), when the *hexabromide* crystallised, or the addition was continued in the usual way and the resulting solution warmed, cooled, and scratched. The *hexabromide* crystallised in small, yellowish-orange prisms, which were dried in a vacuum over phosphorus pentoxide; *m. p.* 117–118° (decomp.) (Found: Br, 68.2.  $\text{C}_{10}\text{H}_8\text{N}_2\text{Br}_6\text{S}_2$  requires Br, 68.6%). The yield was nearly quantitative. The hexabromide showed no change on exposure to air for several hours; on exposure for 5 days, the compound lost appreciable bromine, very slowly becoming red. It was reduced in the usual way by sulphurous acid (*loc. cit.*). It dissolved readily in warm alcohol; on dilution and warming, acetaldehyde was evolved. A pure bromo-substitution derivative could not be isolated.

3 : 5-Diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole.—*s*-Diphenylthiocarbamide (15 g.) dissolved in absolute alcohol (300 c.c.) was gradually treated with bromine until a permanent yellow colour was obtained (Hugershoff, *Ber.*, 1903, **36**, 3121). The solution was filtered from coagulated sulphur into cold water (5 vols.), and the mixture made strongly alkaline with ammonia ( $d$  0.880); the compound then separated in brittle, white granules. On crystallisation from ether, the thiodiazole separated in white plates, m. p. 136°, as recorded in the literature (yield, about 60%).

3 : 5-Diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole Octabromide.—The thiodiazole (1 g.) dissolved in chloroform (10 c.c.) was gradually treated with bromine (1 c.c.), and the resulting solution warmed and kept  $\frac{1}{2}$  hour. On scratching, the octabromide separated in glistening, orange-red prisms, which were dried in a vacuum over potassium hydroxide; m. p. 103–105° (Found: Br, 66.2.  $C_{26}H_{20}N_4Br_8S$  requires Br, 66.6%). The bromide dissolved in glacial acetic acid, giving a solution which became colourless and evolved bromine and hydrogen bromide on prolonged boiling. The solution, on being made alkaline, furnished a product which crystallised from alcohol, on persistent scratching, in minute prisms, m. p. 200° (decomp.; after sintering at 110°). The quantity was much too small for investigation, but the product was doubtless an impure bromo-substitution derivative (*loc. cit.*).

3 : 5-Diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole Hexaiodide.—The thiodiazole (3.8 g.) dissolved in 20 c.c. of glacial acetic acid was gradually added to a warm solution of iodine (5 g.) in the same solvent (250 c.c.), and the resulting solution warmed and kept for 3 hours; a part of the iodo-additive compound then separated in small, black, glistening prisms, which were washed with a little acetic acid and dried in a vacuum; m. p. 120°. A second crop separated over-night in shining, black prisms having a dark green reflex, which were thoroughly washed with glacial acetic acid and dried in a vacuum as before; m. p. 122° (decomp.) (Found: I, 66.5.  $C_{26}H_{20}N_4I_6S$  requires I, 66.8%).

The hexaiodide was practically unacted upon by sulphurous acid owing to its insolubility, but was readily reduced by sulphur dioxide in acetic acid solution. It was readily decolorised by sodium thiosulphate [0.1120 g. in glacial acetic acid (redistilled over potassium permanganate) required 27.5 c.c. of 1.97*N*/100-sodium thiosulphate. I, 57.4%]. The iodide was readily soluble in ether, ethyl acetate, and alcohol, but could not be recrystallised.

A number of experiments were also carried out on the halogenation of 3 : 5-di-*p*-tolylimino-2 : 4-di-*p*-tolyltetrahydro-1 : 2 : 4-thiodiazole, m. p. 138°, which was obtained in the same way as the

phenyl derivative (Hugershoff, *loc. cit.*), but definite compounds could not be isolated; bromination and iodination in different solvents and under various conditions led to uncrystallisable gums or resins.

The author desires to express his gratitude to Professor J. F. Thorpe, F.R.S., for the kind interest he has taken in this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

LONDON, S.W. 7.

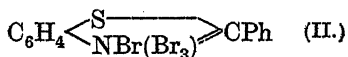
[Received, November 11th, 1925.]

## LXXII.—Bromination of some 5-Substituted 1-Phenylbenzthiazoles.

By ROBERT FERGUS HUNTER.

THE bromination of 1-phenylbenzthiazole has been investigated by Bogert and Abrahamson (*J. Amer. Chem. Soc.*, 1922, **44**, 826), who obtained a red unstable tetrabromo-additive compound, to which they assigned the constitution (I), which on boiling with dilute acetic acid yielded 5-bromo-1-phenylbenzthiazole.

The tetrabromide thus prepared gradually loses bromine on exposure to air, becoming almost colourless, and is instantaneously reduced to 1-phenylbenzthiazole by sulphurous acid and sodium bisulphite (compare J., 1925, **127**, 1319, 1488, 2023). The compound must therefore be a *perbromide*; and may have the constitution (I) or (II), the latter being analogous to that of the tetrabromides of pyridine and quinoline (Trowbridge, *J. Amer. Chem. Soc.*, 1897, **19**, 558; Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124).

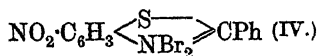
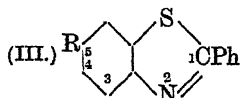


The formation of a *di-iodo*-additive compound and not a *tetraiodo*-derivative by 1-phenylbenzthiazole (*loc. cit.*) is in favour of the formula (I); the slight ionisation of 1-phenylbenzthiazole tetrabromide in glacial acetic acid solutions is, moreover, in accordance with the presence of a "thiazonium" sulphur atom as in (I), but the question cannot be fully discussed until the behaviour of substances such as dimethyl sulphide dibromide (Cahours, *Annalen*, 1865, **135**, 355) has been thoroughly reinvestigated.

The passage of phenylbenzthiazole tetrabromide into 5-bromo-1-phenylbenzthiazole (Bogert and Abrahamson, *loc. cit.*) suggests that there is probably an intimate connexion between the ring nitrogen atom (2) of the fused thiazole nucleus and the carbon atom (5) of the homocyclic ring of the benzthiazole system. The transformation is indeed a sort of "para-migration," and no doubt takes

place by way of a para-bridged intra-annular phase of the benzene ring. It might be expected, therefore, that the substitution of groups of varying polar character on the carbon atom (5) would have a profound effect on the unsaturation of the nitrogen atom (2) as exhibited by a tendency towards the formation of bromo-additive compounds (compare also Fries, *Annalen*, 1906, **346**, 128). It is, moreover, clear that this effect will manifest itself whether the tetrabromide has the constitution (I) or (II), for in the former case the effect on the nitrogen atom (2) will be communicated to the sulphur atom (7) by way of the well-known alternation of affinity effect in carbon chains.

Actually, it was found in connexion with the 5-substituted 1-phenylbenzthiazoles (III) that the electro-polar character of the 5-substituent has a remarkable effect on the tendency of these bases to form bromo-additive compounds.



Thus the negative nitro-group ( $\text{R} = \text{NO}_2$ ) in 5-nitro-1-phenylbenzthiazole depresses the unsaturation of the thiazole system to such an extent as to render the formation of bromo-additive compounds impossible in acetic acid solutions, and to allow the formation only with considerable difficulty of the dibromide (IV) in chloroform. The less negative bromine atom in 5-bromo-1-phenylbenzthiazole ( $\text{R} = \text{Br}$ ), on the other hand, allows the formation of a very unstable tetrabromo-additive compound with difficulty; whilst the positive amino-group ( $\text{R} = \text{NH}_2$ ) enhances unsaturation of the thiazole system in 5-amino-1-phenylbenzthiazole to such an extent as to cause the immediate formation of a stable tetrabromide in the case of the latter benzthiazole derivative.

Bromination of 1-phenylbenzthiazole in chloroform gave rise to two isomeric forms of the tetrabromo-additive compound (m. p.  $126^\circ$  and  $153^\circ$ ), just as di- $\beta$ -naphthylthiocarbamide yields two forms of the hexabromide of 2- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole (Hunter, J., 1925, **127**, 2273). Both forms of the tetrabromide were reduced by sulphurous acid and passed into the substitution derivative on boiling with dilute alcohol and acetic acid (*loc. cit.*). It is highly probable that the lower-melting tetrabromide is identical with that formed in the bromination of the phenylbenzthiazole in glacial acetic acid solution, which usually commences to sinter at about  $130^\circ$ .

The bromo-additive compounds of the benzthiazole series, like the *p*-bromophenyltrimethylammonium perhalides (Reade, J.,



1924, 125, 150), decompose rapidly at the temperature of fusion (and frequently below this: J., 1925, 127, 2026), and therefore the melting point is not a real criterion of purity. For this reason, too much stress cannot be laid on the isolation of isomeric forms of the compounds, for the melting point (which is also the decomposition point) is appreciably affected by the crystalline form of the compound.\* It is hoped to investigate this question more fully at an early date.

#### EXPERIMENTAL.

1-Phenylbenzthiazole was prepared from benzyldeneaniline by Bogert and Abrahamson's method (*loc. cit.*). The finely crushed melt was added in a slow stream to boiling 60% sulphuric acid, and the resulting mixture boiled for an hour (water being added to make up for that lost by evaporation). The acid extract was filtered into cold water (10 vols.), and the precipitated base was washed, dried at 70°, dissolved in the minimum of boiling alcohol (to remove resinous material), and the filtered solution poured into cold water. The product, after drying, crystallised from light petroleum-alcohol (3:1) in pale yellow prisms, m. p. 114°, having the odour of geraniums and other properties described by Hofmann (*Ber.*, 1879, 12, 2359).

*Bromination.* (A). Phenylbenzthiazole (2 g.) dissolved in glacial acetic acid was gradually treated with bromine (Bogert and Abrahamson, *loc. cit.*). The tetrabromide separated in red needles or prisms, which were dried in a vacuum over potassium hydroxide; m. p. 137° after sintering at 130° (Found: Br, 60.6. Calc., Br, 60.3%). On boiling with dilute acetic acid or alcohol, 5-bromo-1-phenylbenzthiazole was produced which crystallised from glacial acetic acid in shining prisms, m. p. 152°.

Since this method of preparing the tetrabromide invariably gave resinous products, the bromination of 1-phenylbenzthiazole in chloroform was examined.

(B). Phenylbenzthiazole (2 g.) dissolved in chloroform (30 c.c.) was gradually treated with bromine (2 c.c.), and the resulting solution boiled, and cooled in ice. On scratching, reddish-brown needles of phenylbenzthiazole tetrabromide separated which were dried in a vacuum over potassium hydroxide; m. p. 126° (decomp.) (Found: Br, 60.6.  $C_{13}H_9NBr_4S$  requires Br, 60.3%). The filtrate from this compound, on concentration and cooling, furnished slender, orange needles of a second *tetrabromide*, which were dried as before; m. p. 153° (decomp.) (Found: Br, 59.8%).

\* Thus specimens of 1-anilinobenzthiazole tetrabromide crystallised from chloroform under different conditions may have melting points anywhere between 112° and 117° (Hunter, J., 1925, 127, 2025).

5-Nitro-1-phenylbenzthiazole was obtained by the direct nitration of phenylbenzthiazole with nitric acid (*d* 1.5) and by nitration with a mixture of sulphuric acid and nitric acid (*d* 1.4) as described in the literature (*loc. cit.*). After two crystallisations from glacial acetic acid, the nitrobenzthiazole was obtained in small, orange prisms, *m. p.* 188°. In both cases the yield exceeded 90%.

5-Nitro-1-phenylbenzthiazole Dibromide.—5-Nitro-1-phenylbenzthiazole was recovered unchanged after a saturated solution of the compound in glacial acetic acid had been treated with bromine. The nitrophenylbenzthiazole (2 g.) suspended in chloroform (40 c.c.) was gradually treated with bromine (2 c.c.); after  $\frac{1}{2}$  hour, the mixture was boiled and filtered, and the filtrate kept over-night. The somewhat pasty precipitate of the dibromide was collected and agitated with an ethereal solution of bromine, when vermilion prisms were obtained which were dried in the usual way. They softened at 120° and melted at 144° (Found: Br, 37.8.  $C_{13}H_8O_2N_2Br_2S$  requires Br, 38.5%). The dibromide lost bromine on exposure to air and was reduced by sulphurous acid in the usual way. On boiling with dilute acetic acid, bromine was evolved with regeneration of the original nitrobenzthiazole.

5-Bromo-1-phenylbenzthiazole Tetrabromide.—When 5-bromo-1-phenylbenzthiazole (1 g.) in chloroform (12 c.c.) was gradually treated with bromine (1.6 c.c.), a dark red solution was obtained which deposited red prisms of a tetrabromo-additive compound, *m. p.* 206–208° (decomp.) (Found: Br, 64.8.  $C_{13}H_8NBr_5S$  requires Br, 65.6%). This compound was most unstable and lost bromine immediately on exposure to air; bromine was also eliminated with regeneration of the original 5-bromo-substitution derivative by boiling with dilute acetic acid, or by treating with sulphurous acid. By using a smaller quantity of bromine, red needles of another bromide were obtained which changed colour at 85°, became orange at 110°, and showed signs of loss of bromine at 175°; *m. p.* 208° (decomp.). The bromine content was that of a tribromo-additive compound [Found: Br, 60.9.  $(C_{13}H_8NBr_4S)_2$  requires Br, 60.4%]. This bromide had similar properties to the tetrabromide already described; it was converted into 5-bromo-1-phenylbenzthiazole by sulphurous acid or by boiling dilute acetic acid.

5-Amino-1-phenylbenzthiazole, prepared by reduction of the 5-nitro-derivative (*loc. cit.*), on repeated crystallisation from boiling aniline or toluene, was obtained in small prisms, *m. p.* 208°, as recorded. In cases where the reduction had proceeded too vigorously, the product after crystallisation was very dark and resinous; attempts were therefore made to work up the base by way of the benzyldene derivative (*loc. cit.*). The product separated from

alcohol in pale yellow plates, m. p.  $190^{\circ}$  ( $39^{\circ}$  above the recorded temperature); the m. p. was unaltered by recrystallisation. 5-Benzylideneamino-1-phenylbenzthiazole prepared from pure 5-amino-1-phenylbenzthiazole had the melting point of  $151^{\circ}$  recorded in the literature. The nature of the high-melting product has not yet been investigated.

*5-Amino-1-phenylbenzthiazole Tetra-bromide.*—5-Amino-1-phenylbenzthiazole (1 g.) suspended in chloroform (30 c.c.) was gradually treated with bromine (1.1 c.c.) dissolved in a small amount of the same solvent; an ochre-coloured precipitate of the bromo-additive compound appeared on the addition of the first drop of halogen. The mixture was boiled and filtered, the residue digested with dry ether containing bromine, and the product dried in the usual way. A dark brown, microcrystalline powder was thus obtained which melted at  $216^{\circ}$  after showing colour change between  $180^{\circ}$  and  $190^{\circ}$  (Found: Br, 60.1.  $C_{13}H_{10}N_2Br_4S$  requires Br, 58.6%). The filtrate from this bromide, on slight concentration, furnished red prisms of another *tetra-bromide*, m. p.  $210$ – $211^{\circ}$ , which were dried in a vacuum as before (Found: Br, 60.3%). The brown *tetra-bromide* was remarkably stable to air and in this respect resembled the dibromide of 4'-amino-1-phenyl-5-methylbenzthiazole (J., 1925, 127, 1318). On boiling with acetic acid a red solution was obtained which deposited prisms of the second *tetra-bromide*, m. p.  $210^{\circ}$ . Both bromides were reduced in the usual way by sulphurous acid, etc. On boiling the red crystals with dilute acetic acid, a dark product was obtained; this was digested with dilute alkali, dried, and repeatedly extracted with boiling alcohol, which removed a purple impurity. The brown residue was washed with ether and dried. It appeared to be an impure bromo-substitution product and softened at about  $170^{\circ}$ ; its analysis corresponded most closely with a *dibromo*-derivative (Found: Br, 39.3.  $C_{13}H_9N_2Br_2S$  requires Br, 41.8%). The purple alcoholic extracts on evaporation furnished a quantity of dark-coloured product insufficient for investigation.

The experiments here described were commenced early in 1924 with the object of studying the effect of the substitution of groups of varying polar and spatial character on the unsaturation of the fused thiazole nucleus. Since the work has been temporarily abandoned, it has seemed desirable to publish the results so far obtained.

The author desires to express his gratitude to Professor J. F. Thorpe and Dr. M. A. Whiteley for the kind interest they have taken in this work.

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LXXIII.—*Studies in Colour and Constitution. Part I.*  
*The Influence of the Methylthiol Group, alone and*  
*in Conjunction with the Methoxy-group.*

By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY.

THE superior bathochromic influence of the methylthiol group in comparison with the methoxy-group was discovered by Brand (*Ber.*, 1909, 42, 3463). The work of Waldron and Reid (*J. Amer. Chem. Soc.*, 1923, 45, 2399) and of Foster and Reid (*ibid.*, 1924, 46, 1936), however, indicated this influence was stronger or weaker than that of the methoxy-group according as the methylthiol group was in the para- or ortho-position with respect to it.

Dyes were prepared from 2- and 4-thioanisidines by one of the authors (H. H. H.) in 1918 (Brit. Pat. 235334 of 1924), and his study of meta-halogenated phenols has afforded the opportunity of comparing the bathochromic effects of the methylthiol and methoxy-groups in ortho- and para-positions, and vice versa, in the same amine.

For this purpose, the action of sodium disulphide on 3-chloro-2-, -4-, and -6-nitrophenols (Hodgson and Moore, *J.*, 1925, 127, 1925) has been investigated. No replacement of chlorine in the free phenols and in 3-chloro-2-nitroanisole took place, but the methyl ethers of 3-chloro-4- and -6-nitrophenols were readily converted into disulphides. These ethers were prepared in good yield by Haworth and Lapworth's method (*J.*, 1923, 123, 2986) and have been described by Hodgson and Moore (this vol., p. 157). Conversion of the disulphides into thioethers and subsequent reduction produce respectively 4-anisidine-2- and 2-anisidine-4-methyl thioethers, in which the positions of the methoxy- and methylthiol groups are interchanged.

Azo-dyes were prepared from the above amines with Schäffer salt, R-salt, and H-acid (in alkaline solution) as second components, and also, for comparison purposes, from 2- and 4-anisidines and 2- and 4-thioanisidines. From the dyeings on wool, the colorimetric estimation of the dye solutions by the Lovibond tintometer, and the colours given by the solid dyes with concentrated sulphuric acid, the superiority of the bathochromic influence of the methylthiol group in the para-position was found to be most pronounced. The methoxy-group in the Schäffer and R-salt dyes, however, exhibited the converse influence, i.e., it produced the optimum effect when it was in the ortho-position. The *o*-methylthiol and *p*-methoxy-groups appear to produce the same effect. The maximum effect was obtained with the *p*-methylthiol group in conjunction with an

*o*-methoxy-group, viz., very pronounced violet colour with the Schäffer and R-salt dyes and an almost indigo-blue colour with the H-acid dye. Chlorine exerts the same influence as the methylthiol group, but to a less degree; the shades, however, are brighter. In all cases the dyes from 4-thioanisidine are the strongest in tinctorial power.

#### EXPERIMENTAL.

**3-Chloro-4- and -6-nitroanisoles.**—The respective chloronitrophenols (8 g.) dissolved in xylene (40 c.c.) were heated under reflux on the water-bath for 8 hours in presence of potassium carbonate (10 g.), and methyl sulphate (10 c.c.) was gradually added. The mixture was rendered strongly alkaline and steam-distilled; xylene and a little ether passed over first and were followed by the main bulk (yield 7 g.; 81%).

**4-Chloro-2- and 2-Chloro-4-anisidines.**—The above ethers (1 g.) were each heated under reflux on the water-bath with concentrated hydrochloric acid (5 c.c.) and water (15 c.c.), with gradual addition of granulated tin (3 g.). After the ether had dissolved, the mixture was made alkaline and the products were removed by steam distillation. For convenience, the hydrochlorides were prepared (yield 0.8 g.). They formed long needles, m. p. 238° and 228°, respectively (Found: Cl, 36.4 and 36.5.  $C_7H_8ONCl \cdot HCl$  requires Cl, 36.6%).

**2:2'-Dinitro- and 4:4'-Dinitro- 5:5'-dimethoxydiphenyl Disulphides.**—3-Chloro-4- and -6-nitroanisoles (8 g.) were each dissolved in alcohol (50 c.c.) and gently boiled under reflux during the cautious addition of aqueous sodium disulphide (crystallised sodium sulphide, 6 g.; sulphur, 0.8 g.; water, 40 c.c.); heating was then continued for 4–5 hours. The respective disulphides separated and the contents were filtered hot, unchanged nitroanisole being removed by warm alcohol (yield 6.5–7 g.; 88–90%).

**2:2'-Dinitro-5:5'-dimethoxydiphenyl disulphide** is insoluble in water, alcohol, or benzene, but soluble in carbon disulphide or glacial acetic acid, from which it crystallises in white needles, m. p. 152° (uncorr.); these rapidly turn yellow in sunlight (Found: N, 7.4; S, 18.0.  $C_{14}H_{12}O_6N_2S_2$  requires N, 7.6; S, 17.4%). The last trace of free sulphur was retained even after repeated crystallisation. Concentrated aqueous or alcoholic alkali hydroxides give violet-red solutions. Concentrated sulphuric acid gives a pale yellow solution in the cold, unchanged by moderate heating or dilution. Chlorosulphonic acid gives a crimson solution in the cold, which becomes yellow on heating and remains so on dilution, whilst oleum (23%  $SO_3$ ) produces a brownish-yellow colour, which

changes to yellow on heating and lemon-yellow on subsequent dilution.

*4:4'-Dinitro-5:5'-dimethoxydiphenyl disulphide* resembles the preceding isomeride in solubility. It crystallises from glacial acetic acid in white, glistening micro-plates, m. p.  $194^{\circ}$  (uncorr.) (Found : N, 7.6; S, 17.9%). The solutions in alkalis are deep red. Concentrated sulphuric acid produces an orange-yellow colour in the cold, which becomes successively red, brown, and green on heating, and brownish-purple on subsequent dilution. Chlorosulphonic acid or oleum (23%) produces a green colour in the cold, which changes to reddish-brown on heating; a reddish-brown precipitate forms on dilution.

*2-Nitro- and 4-Nitro-5-methoxythioanisoles.*—The above disulphides (2 g.) were each heated on the water-bath for 15 minutes with alcohol (10 c.c.), crystallised sodium sulphide (1 g.), sodium hydroxide (2.4 g.), and water (10 c.c.). The mixture was then stirred into water (35 c.c.), filtered if necessary, and warmed with methyl sulphate (2–2.5 c.c.), when the thioanisole separated (yield 2 g.; 92%).

*2-Nitro-5-methoxythioanisole* is insoluble in cold but slightly soluble in hot water and is very slowly volatile in steam. It crystallises from alcohol in yellow needles, m. p.  $112$ – $113^{\circ}$  (uncorr.), and is very slowly decomposed by nitric acid (Found : N, 7.2.  $C_8H_9O_3NS$  requires N, 7.0%). The crimson solution in concentrated sulphuric acid becomes violet on heating and thereafter yellow on dilution. The corresponding colorations produced by oleum (23%) and chlorosulphonic acid are blood-red, reddish-brown and yellow, and blue, violet and yellow, respectively.

*4-Nitro-5-methoxythioanisole* resembles the preceding isomeride in solubility and volatility in steam, but crystallises from alcohol in paler yellow needles, m. p.  $79$ – $80^{\circ}$  (uncorr.) (Found : N, 6.9%). The colorations produced by solution, heating, and subsequent dilution are : for concentrated sulphuric acid, scarlet, blood-red to reddish-violet, blood-red; for oleum, chocolate-brown, blood-red, yellow; for chlorosulphonic acid, red, orange, yellow.

*2-Anisidine-4-methyl- and 4-Anisidine-2-methyl Thioethers.*—The respective nitro-compounds (2 g.) were heated under reflux with granulated tin (4 g.), concentrated hydrochloric acid (10 c.c.), and water (10 c.c.) until all had dissolved. The solution was made distinctly alkaline with sodium hydroxide and steam-distilled. In both cases, the bases passed over as oils, but only 2-anisidine-4-methyl thioether crystallised on standing. The 4-anisidine isomeride was converted into the hydrochloride.

*2-Anisidine-4-methyl thioether* is very soluble in alcohol and

crystallises from water in white, feathery needles, m. p.  $44^{\circ}$  (uncorr.), which become discoloured in air (yield 1.3 g.; 77%) (Found: N, 8.5; S, 19.1.  $C_8H_{11}ONS$  requires N, 8.3; S, 18.9%). Concentrated sulphuric acid gives a yellow solution which remains unchanged on heating or dilution. The pale violet solution in oleum changes to deep violet on warming, but becomes colourless on prolonged heating.

The *hydrochloride* crystallises from hydrochloric acid in colourless needles which turn pink in air; m. p.  $235^{\circ}$  (approx.) (Found: Cl, 17.5; S, 15.2.  $C_8H_{11}ONS, HCl$  requires Cl, 17.3; S, 15.6%).

4-Anisidine-2-methyl thioether is an oil which is very soluble in alcohol, but only slightly so in water. Concentrated sulphuric acid gives a violet solution in the cold, which becomes reddish-violet on heating. The corresponding colorations with oleum and chloro-sulphonic acid are blue-violet and reddish-purple and purple and reddish-purple, respectively.

The *hydrochloride* forms white needles, m. p.  $210-211^{\circ}$ , which become steel-grey on exposure to light (Found: N, 7.4; Cl, 17.25; S, 15.3.  $C_8H_{11}ONS, HCl$  requires N, 7.0; Cl, 17.3; S, 15.6%).

*The Dyes.*—These were prepared in the usual way and sodium chloride was removed as completely as possible.

*Dyeing trials.* Wet strips of wool (2.5 g.) were introduced into a bath of water (250 c.c.) containing the dyes (0.025 g.), sodium sulphate (0.25 g.), and sulphuric acid (0.05 g.). The solution was gradually heated to the boiling point and there maintained until the dyeing was complete.

*Dye solutions.* These were evaluated in terms of red, yellow, and blue components by means of the Lovibond tintometer.

The colours produced by sulphuric acid on the dry dye powders were also examined.

For convenience, the dyes are referred to by the attached numerals, which indicate the particular amine employed: 2-anisidine (I), 4-anisidine (II), 4-chloro-2-anisidine (III), 2-chloro-4-anisidine (IV), 2-anisidine-4-methyl thioether (V), 4-anisidine-2-methyl thioether (VI), 2-thioanisidine (VII), 4-thioanisidine (VIII).

The order of increasing redness is from left to right.

### Results.

Dye.	Experiment.	Order.
From Schäffer Salt.	Wool dyeing.	V, VIII, I, III, VII, IV, II, VI. (Red-violet) (Red) (Scarlet to orange)
" " "	Lovibond.	V, VIII, VI, III, I, IV, VII, II.
" " "	Sulphuric acid.	VIII, V, VII, VI, IV, II, III, I. (Blue) (Violet) (Crimson)
" R-Salt.	Wool dyeing.	V, VIII, III, I, VI, II, VII, IV. (Violet) (Bluish-red) (Red with gradual increase of yellow)

Dye.	Experiment.	Order.
From R-Salt.	Lovibond.	V, VIII, III, I, VI, IV, II, VII.
" "	Sulphuric acid.	VIII, V, VII, VI, IV, II, III, I. ( Blue ) ( Violet ) ( Crimson )
" H-Acid.	Wool dyeing.	V, VIII, VI, II, VII, III, IV, I. (Indigo-blue) ( Red-violet ) ( Violet-red )
" "	Lovibond.	V, VI, VII, VIII, IV, I, II, III.
" "	Sulphuric acid.	VIII, V, IV, VI, II, III, I, VII. ( Blue ) ( Violet )

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## LXXIV.—*Iodination in the Carbazole Series.*

By STANLEY HORWOOD TUCKER.

OXIDATION of carbazole brought about the formation of the two dicarbazyls described by Perkin and Tucker (J., 1921, 119, 216). Attempts to synthesise these compounds and their possible isomerides have led to the preparation of iodo-derivatives of carbazole and of its alkyl and acyl compounds. Except the iodo-compounds described by Stevens and Tucker (J., 1923, 123, 2146) and Tucker (J., 1924, 125, 1144), the only one prepared was di-iodocarbazole (Classen, D.R.-P. 81929, 1894). Classen's description of it is inaccurate.

3-Iodocarbazole has been synthesised from 3-aminocarbazole (Tucker, *loc. cit.*). It has now been obtained directly from carbazole by the action of potassium iodide and iodate in glacial acetic acid solution, working according to the equation  $3C_{12}H_9N + 2KI + KIO_3 + 3CH_3 \cdot CO_2H = 3C_{12}H_8NI + 3H_2O + 3CH_3 \cdot CO_2K$ , except that potassium iodate and acetic acid are used in excess. The iodine at first liberated is gradually used up and the solution finally becomes colourless. The 3-iodocarbazole so obtained is mixed with considerable quantities of di-iodocarbazole. Much of the 3-iodocarbazole can be separated by crystallisation, but to obtain the di-iodocarbazole it is necessary to utilise the acetyl or benzoyl derivative.

The di-iodocarbazole described by Classen, and prepared by a different method from the above, was alleged to be yellow, and to melt at 184°; repetition of his work gave only colourless di-iodocarbazole, m. p. 202–204°. The di-iodocarbazole is almost cer-



tainly 3 : 6-di-iodocarbazole by analogy with other disubstitution products of carbazole.

Iodination of 9-methyl and 9-ethylcarbazole by the above method likewise gives the respective 3-iodo- and di-iodo-compounds.

Like carbazole and the 9-alkylcarbazoles, 9-benzoylcarbazole may be iodinated by means of potassium iodide and iodate in glacial acetic acid to give a corresponding yield of its 3-iodo-derivative, but the discharge of the iodine coloration is much less rapid, viz., 10 minutes for carbazole (less for the 9-alkylcarbazoles) and 75 minutes for 9-benzoylcarbazole. Incomplete iodination of 9-toluene-*p*-sulphonylcarbazole took place under similar conditions in 2 hours. Iodination of 9-acetylcarbazole did not proceed to any appreciable extent. Judged, therefore, by this process of iodination, resistance to replacement of hydrogen in the carbazole nucleus increases in the order 9-alkylcarbazoles, carbazole, 9-benzoyl-, 9-toluene-*p*-sulphonyl-, and 9-acetyl-carbazole. All may be iodinated by the action of the more vigorous iodinating reagent, iodine and nitric acid in glacial acetic acid (Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 292). The 9-alkylcarbazoles and carbazole give at once idonitro-compounds.

There is no evidence of the formation of any 1-iodo-derivatives.

#### EXPERIMENTAL.

*Iodination of Carbazole.*—(i) *Using potassium iodide and potassium iodate in glacial acetic acid.* Pure \* carbazole (16.7 g.) was dissolved in boiling glacial acetic acid (250 c.c.), and potassium iodide (11 g.) added. The solution was cooled somewhat, finely-powdered potassium iodate (16 g., i.e., approximately twice the amount theoretically required) added, and the mixture then boiled until it acquired a clear straw-coloured tint (10 minutes). The hot solution was decanted from the undissolved potassium iodate and allowed to cool slowly to 45°. The faintly brown, nacreous plates which separated were rapidly filtered off and recrystallised from glacial acetic acid (or alcohol), the solution being allowed to cool to 45° and filtered as before from the white, nacreous plates (10–12 g.) of 3-iodocarbazole, m. p. 192–194°. From the united filtrates, on standing, there separated 3 : 6(?)*-di-iodocarbazole*, m. p. 202–204° (Found : I, 60.6.  $C_{12}H_7NI_2$  requires I, 60.6%), but since the

\* The yield of 3-iodocarbazole is considerably diminished if the carbazole used is impure. Pure carbazole exhibits a faint violet fluorescence, and melts at 238° when the melting point is taken in the usual way with a long emergent stem; when taken with a short Anschütz thermometer having the stem immersed, the m. p. is 245° (compare Graebe and Glaser, *Ber.*, 1872, **5**, 12; Täuber, *ibid.*, 1891, **24**, 2597; Kirby, *J. Soc. Chem. Ind.*, 1921, **40**, 274r; Senseman and Nelson, *Ind. Eng. Chem.*, 1923, **15**, 382).

quantity was very small it was found better to proceed thus: The united filtrates were poured into water and the white precipitate was dried (16.5 g.). Crystallisation of this product from various solvents did not raise the melting point above 160°. Accordingly, the material was boiled with acetic anhydride and a trace of concentrated sulphuric acid. After a short time, a white, crystalline precipitate suddenly separated. It was washed with boiling glacial acetic acid and recrystallised several times from benzene. 3:6(?)*-Di-iodo-9-acetylcarbazole* was thus obtained in long, colourless needles, grouped in porcupine-like tufts, m. p. 224—225° (Found: I, 55.4.  $C_{14}H_9ONi_2$  requires I, 55.1%). The acetic anhydride filtrate was poured into water, and the precipitate produced was crystallised from glacial acetic acid. Colourless needles separated in rosettes very like those of 3-iodo-9-acetylcarbazole (m. p. 145—147°), but repeated crystallisation from glacial acetic acid, alcohol, and benzene—light petroleum failed to raise the melting point above 133—137°. However, by boiling this material with alcoholic potassium hydroxide solution for a few minutes, pouring into water, and recrystallising the precipitate from glacial acetic acid as described under the isolation of 3-iodocarbazole, a good yield of pure 3-iodocarbazole was obtained.

The separation of 3-iodocarbazole and 3:6-di-iodocarbazole can also be effected by benzoylation.\* The product (16.5 g., obtained after removal of 3-iodocarbazole by preliminary crystallisation) was dissolved in acetone (100 c.c.), and powdered potassium hydroxide (12 g.) added. The mixture was boiled, allowed to cool slightly, and benzoyl chloride (10 c.c.) added slowly; a vigorous reaction took place. The liquid was swirled round after each addition of benzoyl chloride, but not shaken vigorously until the end; it was then poured into water. The pale brown oil at first precipitated, which solidified to a pasty, white solid, was dissolved in acetone. The crystals which separated were much less soluble in acetone than the crude material, and were best recrystallised

\* The method of benzoylation of carbazole (Stevens and Tucker, *loc. cit.*, p. 2146) proceeds as given for the quantities used, but with larger quantities of carbazole (16.7 g., e.g.) vigorous shaking must be avoided; the liquid, after addition of benzoyl chloride, should be gently swirled, and only shaken finally. (The author is indebted to Mr. A. Kent, M.A., B.Sc., of this Department, for this observation.) To separate 9-benzoylcarbazole from unchanged carbazole, the mixture is dissolved in benzene and allowed to cool; carbazole then separates, and more is obtained by concentrating the filtrate to half-bulk. The benzene (in which 9-benzoylcarbazole is very soluble) is evaporated and the residue crystallised from much alcohol. Pure 9-benzoylcarbazole, m. p. 98°, is obtained. If carbazole is not thus removed, the m. p. of the product does not rise above 90° even after repeated crystallisation. The above applies generally to all benzoylations described in this paper.

from pyridine to which a drop of water was added, or from carbon tetrachloride, giving 3 : 6-di-iodo-9-benzoylcarbazole, m. p. 204—205° (Found : I, 48.9.  $C_{19}H_{11}ONI_2$  requires I, 48.6%). Concentration of the acetone filtrate gave a further crop, the total yield of pure material being 3.2 g. The very concentrated acetone filtrate deposited 3-iodo-9-benzoylcarbazole (0.8 g.), m. p. 145—146° (Found : I, 31.9.  $C_{19}H_{12}ONI$  requires I, 32.0%). A thick, brown oil was left. When macerated with cold glacial acetic acid, much dissolved; but a yellow powder remained insoluble. After several crystallisations from carbon tetrachloride or light petroleum, it melted at 184—186°, but appears to be 3-iodocarbazole (0.2 g.).

(ii) *Using iodine and yellow mercuric oxide in alcohol* (Classen, *loc. cit.*). Classen's procedure was followed as described, then the product was recrystallised three times from carbon tetrachloride, and red crystals were obtained, m. p. 201—204°. These were boiled in glacial acetic acid with animal charcoal, and recrystallised from alcohol in colourless, long, rectangular laminæ of 3 : 6-di-iodocarbazole, m. p. 202—204°.

**3-Iodo-9-acetylcarbazole.**—The best method of preparing this compound is acetylation of 3-iodocarbazole (Tucker, *loc. cit.*); but it is readily prepared from 9-acetylcarbazole thus : 9-Acetylcarbazole (2 g.) and iodine (1 g.) were dissolved in glacial acetic acid (40—50 c.c.), the solution cooled to about 60°, and a solution of 2 c.c. of concentrated nitric acid in 8 c.c. of glacial acetic acid added drop by drop. When 1 c.c. of the solution had been added, the mixture was boiled and the addition of the nitric acid solution continued at intervals during the boiling until the iodine coloration had just vanished. Yellow crystals separated on cooling. They recrystallised from glacial acetic acid, and from alcohol, in colourless crystals, slightly soluble in light petroleum. Attempts to iodinate 9-acetylcarbazole by means of iodide and iodate, as for the iodination of carbazole, showed that after several hours' boiling some iodine had been used up, but no iodo-compounds could be isolated.

3 : 6(?)*-Di-iodo-9-acetylcarbazole* was prepared from 3 : 6(?)*-di-iodocarbazole* by boiling with acetic anhydride containing a trace of concentrated sulphuric acid. The solution set at once to a pure white solid, which crystallised from benzene, much glacial acetic acid, or alcohol in clusters of long needles, m. p. 224—225°. It was readily hydrolysed by boiling alcoholic potassium hydroxide solution to 3 : 6-di-iodocarbazole.

**3-Iodo-9-benzoylcarbazole** was prepared (a) from 3-iodocarbazole by the method described under the separation of 3-iodocarbazole and 3 : 6-di-iodocarbazole. Using theoretical quantities (2.9 g. of 3-iodocarbazole, 1.4 g. of benzoyl chloride, and 0.6 g. of solid

potassium hydroxide in 20 c.c. of acetone), the yield was practically as good. Twenty-five per cent. of the 3-iodocarbazole was recovered; (b) from 9-benzoylcarbazole—(i) 9-Benzoylcarbazole (4 g.), potassium iodide (1.6 g.) and potassium iodate (excess) in glacial acetic acid (40 c.c.) were boiled until the solution became colourless ( $1\frac{1}{2}$  hours). It was then decanted from unchanged iodate into water, and the salmon-pink, powdery solid recrystallised from acetone. The yield of pure 3-iodo-9-benzoylcarbazole was 2.2 g. A small amount, m. p.  $201^{\circ}$ , was obtained from the residues by crystallisation from pyridine. It is therefore probably 3 : 6-di-iodo-9-benzoylcarbazole : (ii) 9-Benzoylcarbazole (5.4 g.) and iodine (2.5 g.) were dissolved in glacial acetic acid (100 c.c.), and a solution of nitric acid in acetic acid was added as in the preparation of 3-iodo-9-acetylcarbazole. The solution became clear in about 20 minutes, was poured into water, and the precipitated yellow solid crystallised from pyridine with addition of a drop of water. The crystals so obtained dissolved in alcohol except a small amount of insoluble, white substance, which, after recrystallisation from pyridine, melted at  $204\text{--}205^{\circ}$  and was 3 : 6-di-iodo-9-benzoylcarbazole. The alcoholic filtrate therefrom deposited 3-iodo-9-benzoylcarbazole. It crystallised well from alcohol, but the crystals were ill-defined and resembled seaweed in shape and arrangement. On certain occasions when the alcoholic solutions were left standing, the crystals assumed a plate shape, but this could not be repeated at will. The acetone solution of 3-iodo-9-benzoylcarbazole deposited clusters of very long needles, which could be removed and were stable out of the solution, whereas the crystals remaining in solution, if scratched, immediately changed into thick, six-sided plates. The acetone solution usually deposited a mixture of needles and plates. Pyridine, in which it is very soluble, and light petroleum, in which it is soluble with difficulty, also gave plate crystals. It is sparingly soluble in glacial acetic acid, but crystallisation therefrom does not purify the substance. Benzene and carbon tetrachloride solutions gave small, colourless crystals. The two crystalline forms mentioned above melted at  $145\text{--}146^{\circ}$ , and a mixed m. p. was unchanged. The substance is therefore dimorphic. Exposure to light turns it faintly brown; a property possessed also by 9-benzoylcarbazole. It is readily hydrolysed to 3-iodocarbazole by alcoholic potassium hydroxide solution.

**3 : 6-Di-iodo-9-benzoylcarbazole.**—3 : 6-Di-iodocarbazole (1 g.) was treated with benzoyl chloride (0.6 g.) and potassium hydroxide (0.5 g.) in acetone (20 c.c.) in the usual way. 3 : 6-Di-iodo-9-benzoylcarbazole was precipitated, and after washing with hot acetone, in which 3 : 6-di-iodocarbazole is very soluble, was obtained

pure (0.8 g.), m. p. 204—205°. A mixed m. p. with 3 : 6-di-iodo-carbazole (m. p. 202—204°) was much lower. It crystallises best from a dilute solution in pyridine, to which a few drops of water are subsequently added, in long rods. It is much less soluble in carbon tetrachloride, and soluble with difficulty in acetone, from which microcrystals are obtained. It is readily hydrolysed by alcoholic potassium hydroxide solution to 3 : 6-di-iodocarbazole.

3-Iodo-9-toluene-*p*-sulphonylcarbazole was prepared thus : (i) 3-Iodocarbazole (1.5 g.), toluene-*p*-sulphonyl chloride (1.0 g.), and potassium hydroxide (0.3 g.) in acetone (10 c.c.) were boiled together for 10 minutes, and poured into water. The precipitated solid crystallised from alcohol, in which it was sparingly soluble, in colourless, diamond-shaped rhombs (1.3 g.), m. p. 170—171° (Found : I, 28.5.  $C_{19}H_{14}O_2NIS$  requires I, 28.4%). 3-Iodocarbazole (0.3 g.) was recovered from the alcoholic filtrate. 3-Iodo-9-toluene-*p*-sulphonylcarbazole is easily soluble in cold pyridine, hot acetone, benzene, glacial acetic acid, ethyl acetate, aniline, or carbon tetrachloride, and less soluble in light petroleum, from all of which it crystallises, but best from acetone, benzene, alcohol-acetone, or alcohol-pyridine. (ii) 9-Toluene-*p*-sulphonylcarbazole\* (2.6 g.) and iodine (0.8 g.) were dissolved in glacial acetic acid (50 c.c.), and a solution of nitric acid in glacial acetic acid (usual strength) was slowly added to the boiling solution. In 10 minutes, about 3 c.c. of the nitric acid solution had been added, and the solution was free from iodine coloration. The pale yellow solution poured into water gave a canary-yellow solid, which was extracted with alcohol. A white, insoluble portion crystallised from much glacial acetic acid in colourless needles, m. p. 257°. It is 3 : 6-di-iodo-9-toluene-*p*-sulphonylcarbazole (Found : I, 43.7.  $C_{19}H_{13}O_2NI_2S$  requires I, 44.3%). The alcoholic extract deposited impure 3-iodo-9-toluene-*p*-sulphonylcarbazole, a substance melting at 175°, and colourless rods melting at 118—121° (Found : I, 11.4; *M*, by Rast's method, 334. A mixture of 9-toluene-*p*-sulphonylcarbazole and 3-iodo-9-toluene-*p*-sulphonylcarbazole,  $C_{19}H_{15}O_2NS + C_{19}H_{14}O_2NIS$ , requires I, 16.5%; *M*, 384).

(iii) 9-Toluene-*p*-sulphonylcarbazole (1 g.) was boiled with potassium iodide (0.34 g.) and excess of potassium iodate in glacial acetic acid (10 c.c.) for several hours, but the iodine coloration did not disappear. In another experiment, using half the quantity of

\* Compare footnote on benzoylation of carbazole. Application of the same method of removal of carbazole after preparation of 9-toluene-*p*-sulphonylcarbazole produced the latter in large, colourless, prismatic crystals, softening at 128°, and giving a clear melt at 133° (compare Cassella, D.R.-P. 224951, 1909; Herz, A.P. 966092, 1910).

potassium iodide, the colour was discharged in  $2\frac{1}{2}$  hours and a nearly theoretical yield of the substance (m. p.  $118-121^\circ$ ) mentioned under (ii) was obtained.

3 : 6 - *Di-iodo-9-toluene-p-sulphonylcarbazole*.—9-Toluene-*p*-sulphonylcarbazole (2.5 g.), iodine (2.0 g.), and glacial acetic acid (50 c.c.) were boiled together during addition of nitric acid in acetic acid (usual strength) until the iodine colour disappeared (45—60 minutes). Before the colour had vanished, needle-shaped crystals began to separate. The mixture was allowed to cool; the separated crystals crystallised from glacial acetic acid and then from benzene in tetrahedral prisms, m. p.  $257^\circ$ . It is only slightly soluble in glacial acetic acid, carbon tetrachloride or acetone, but readily soluble in hot benzene.

*Iodination of 9-Methylcarbazole*.—The methylation of 3-iodo-carbazole has been described (Stevens and Tucker, *loc. cit.*, 2146). Iodination of 9-methylcarbazole was effected as follows : 9-Methylcarbazole (0.8 g.), potassium iodide (0.47 g.), and excess of potassium iodate were boiled in glacial acetic acid (10 c.c.) for 2 minutes, in which time a green solution was obtained. By the usual treatment there were separated in small quantity by means of alcohol 3-iodo-9-methylcarbazole and a product, m. p.  $181^\circ$ . The latter is 3 : 6-*di-iodo-9-methylcarbazole* (Found : I, 58.6.  $C_{13}H_9NI_2$  requires I, 58.7%). It was also prepared by the action of methyl sulphate on 3 : 6-di-iodocarbazole in presence of acetone and solid potassium hydroxide. It is readily soluble in glacial acetic acid, very sparingly soluble in alcohol, and, although sparingly soluble, crystallises from acetone in long, thin rods, m. p.  $181-182^\circ$ .

*Iodination of 9-Ethylcarbazole*.—9-Ethylcarbazole (19.5 g.) and potassium iodide (11.0 g.) were dissolved in glacial acetic acid (200 c.c.), and potassium iodate (16 g.) was added in portions to the hot solution. A gentle reaction set in, and the colour soon gave place to green. The solution was poured into water, and a pasty solid possessing a silky sheen was deposited. This was dissolved in excess of glacial acetic acid. In sufficiently dilute solution, no oil separated, but impure green crystals (11 g.), m. p.  $71^\circ$ . The filtrate from these on concentration deposited colourless crystals, m. p.  $80^\circ$  (3.5 g.). By further concentration, a final crop (5.5 g.) of green crystals, m. p.  $140-144^\circ$ , was obtained. The crystals, m. p.  $80^\circ$ , were purified by recrystallisation from glacial acetic acid or alcohol, and separated in long needles, m. p.  $83-84^\circ$ , identical with 3-iodo-9-ethylcarbazole (Stevens and Tucker, *loc. cit.*). The green crystals, m. p.  $140-144^\circ$ , crystallised from much glacial acetic acid and finally from alcohol in colourless needles, m. p.  $152-153^\circ$ , and were shown to be 3 : 6-*di-iodo-9-ethylcarbazole* (Found :

I, 56.9.  $C_{14}H_{11}NI_2$  requires I, 56.8%). It is only slightly soluble in alcohol or in glacial acetic acid.

3-Iodo-9-isopropylcarbazole was prepared by Mr. W. H. Chalmers, B.Sc., A.I.C., by boiling a mixture of 3-iodocarbazole (2 g.), isopropyl iodide (4 g.), and potassium hydroxide (2 g. in 1 c.c. of water) in acetone (6 c.c.) for 6 hours. The usual procedure, and crystallisation of the product from glacial acetic acid, gave white, silvery leaflets, m. p. 95—97° (Found: I, 38.2.  $C_{15}H_{14}NI$  requires I, 37.9%).

3-Iodocarbazole could not be obtained from carbazole by the action of iodine and nitric acid in glacial acetic acid. It crystallises well from light petroleum, and is very soluble in benzene, pyridine, or acetone. As already stated, it is best crystallised from carbon tetrachloride or glacial acetic acid.

3:6-Di-iodocarbazole, isolated in small yield in the iodination of carbazole, was prepared from carbazole by method (i), using twice the quantity of potassium iodide used to obtain monoiodocarbazole, and proceeding as before. Purification of the pink product was difficult, but it was effected as given under the mercuric oxide experiment, method (ii). It was found best, in order to obtain pure 3:6-di-iodocarbazole, to acetylate or benzoyleate the material (as described above), and hydrolyse the product with alcoholic potassium hydroxide solution. 3:6-Di-iodocarbazole is very soluble in acetone. It crystallises best from glacial acetic acid or alcohol, in long laminae.

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## LXXV.—Optical Activity and the Polarity of Substituent Groups. Part III. Menthyl Acetophenone-o-carboxylate.

By HAROLD GORDON RULE and JOHN SMITH.

IN certain cases it has now been established that the influence of substituents on the optical rotatory power of an organic compound is similar to their influence on acidity. This has been shown to hold true for the condensation products of an optically active base with substituted benzaldehydes (Betti, *Gazzetta*, 1923, 53, 417) and for the menthyl esters of monosubstituted acetic acids (Rule and Smith, *J.*, 1925, 127, 2188).

On the other hand, the menthyl esters of substituted benzoic acids prepared by Cohen reveal an influence of a quite different type. Here the relative changes in rotation produced by a number of simple

ortho-substituents (substitution in the *m*- or *p*-position has little effect) are given by  $\text{NO}_2 > \text{CO}_2\text{H} > \text{H} > \text{I} > \text{CH}_3 > \text{Br} > \text{Cl} > \text{F} > \text{O}\cdot\text{CH}_3$ . As has already been pointed out (Rule, J., 1924, 125, 1122; Rule and Paterson, *ibid.*, 2159), this series is in very close agreement with the relative polarity of the groups as deduced from the molecular inductive capacities of compounds, and with the relative effect of the substituents on the nitration of benzene as we pass from the strongly positive (meta-directive) nitro-group to the strongly negative (para-directive) fluoro-group.

Only two positive groups occur in the above series and, unfortunately, few other simple groups of this type can be readily tested in the case of the menthyl benzoates. Acetophenone-*o*-carboxylic acid, however, is a comparatively accessible compound and figures are available relating to the influence of the acetyl group on benzene substitution.

It has been shown by Camps (compare Holleman, "Die direkte Einführung von Substituenten," 1910, p. 190) that when acetophenone is nitrated at 15° it yields a mixture of about 55% of the *m*-compound and 45% of the *o*-compound. Comparing these figures with those previously quoted for the nitration of nitrobenzene and of benzoic acid (Rule and Paterson, *loc. cit.*), we obtain:

	$\text{NO}_2$ .	$\text{CO}_2\text{H}$ .	$\text{CO}\cdot\text{CH}_3$ .
<i>m</i> -Compound.	93	76	55%

The determination of the relative polarity of the acetyl group from molecular inductive capacity data is inconclusive, as will be seen from the following values ( $\text{X} = \text{CH}_3\cdot\text{CO}$ ):

Series.		Dielec. const.	Density.	Mol. ind. capac.
HX.	Acetaldehyde.	18.5	0.80	10.1
EtX.	Methyl ethyl ketone.	17.8	0.81	15.8
$\text{C}_6\text{H}_5\text{X}$ .	Acetophenone.	18.1	1.03	21.0

On comparing these figures with those calculated by Rule and Paterson (*loc. cit.*), it is found that the *m*-directive groups fall into the order:

Series	HX.	—	CN,	$\text{CO}_2\text{H}$ ,	$\text{CO}\cdot\text{CH}_3$ ,	H.
	EtX.	$\text{NO}_2$ ,	CN,	$\text{CO}\cdot\text{CH}_3$ ,	$\text{CO}_2\text{H}$ ,	H.
	$\text{C}_6\text{H}_5\text{X}$ .	$\text{NO}_2$ ,	CN,	$\text{CO}\cdot\text{CH}_3$ ,	$\text{CO}_2\text{H}$ ,	H.

From the evidence of the benzene substitution data, which is partly supported by that of inductive capacity, it may be concluded that the acetyl group falls between the carboxyl group and hydrogen.

The menthyl ester of acetophenone-*o*-carboxylic acid has now been prepared, and the optical properties of the compound have been



examined for sodium light and that of the three chief mercury lines. Owing to the slight yellow colour of the melt, the rotation of the fused ester could only be determined over the range  $\lambda_D$  to  $\lambda_{gr}$ , but the rotatory power in benzene and in acetone solution was examined over the range  $\lambda_D$  to  $\lambda_{vi}$ . The values of  $1/\alpha$  when plotted against  $\lambda^2$  gave straight lines. In addition, the dispersion ratio  $\alpha_{gr}/\alpha_D$  for the fused ester at  $94^\circ$  and for solutions in benzene and acetone at the ordinary temperature remained approximately constant in the neighbourhood of 1.213. It may therefore be concluded that the compound exhibits normal and apparently simple rotatory dispersion in this region of the spectrum. The molecular rotations were as follows: fused ester,  $[M]_D^{94^\circ} = -261^\circ$ ; in benzene (5%),  $[M]_D^{80^\circ} = -284^\circ$ ; in alcohol (2%),  $[M]_D^{80^\circ} = -267^\circ$ ; in acetone (5%),  $[M]_D^{80^\circ} = -253^\circ$ .

Like other positive *o*-substituents, the acetyl group therefore brings about an increase in the rotation of menthyl benzoate. The influence of various *o*-substituents in this case is summarised in the following table, in which the additional figures for the molecular rotations were determined by Cohen and those for the dispersion ratios by Pickard and Kenyon:

Substit.	NO <sub>2</sub> .	CO <sub>2</sub> H.	CO·CH <sub>3</sub> .	H.	I.	CH <sub>3</sub> .	Br.	Cl.	F.	O·CH <sub>3</sub> .
$[M]_D$	-381*	332†	261†	239	237	231	205	195	194	148
$\alpha_{gr}/\alpha_D$	1.26	1.21	1.21	1.18	1.19	—	—	—	1.18	—
	* At $65^\circ$ .			† In solution.				‡ At $94^\circ$ .		

The remarkably close correspondence between the effect of substituents on the rotatory power of menthyl benzoate (I) and on benzene substitution (II) is seen by a comparison of the series given below, in which the agreement is broken only by a slight displacement of the iodine atom. Series III represents the relative polarity of the substituents as determined from the inductive capacities of compounds.

- I. NO<sub>2</sub> > CO<sub>2</sub>H > CO·CH<sub>3</sub> > H > I > CH<sub>3</sub> > Br > Cl > F > O·CH<sub>3</sub>
- II. NO<sub>2</sub>, CO<sub>2</sub>H, CO·CH<sub>3</sub>, H, CH<sub>3</sub>, Br, I, Cl, F
- III. NO<sub>2</sub>, CO<sub>2</sub>H (?), CO·CH<sub>3</sub>, CO<sub>2</sub>H (?), H, CH<sub>3</sub>, I, Br, Cl, F.

#### EXPERIMENTAL.

Acetophenone-*o*-carboxylic acid was prepared by the method of Gabriel and Neumann (*Ber.*, 1893, 26, 952). Phthalic anhydride, acetic anhydride, and potassium acetate were heated together to give phthalylacetic acid, and the latter, after purification, was converted into acetophenone-*o*-carboxylic acid by heating under pressure with water at  $200^\circ$ . After several recrystallisations from

water, the acid melted sharply at  $112^{\circ}$  (Gabriel and Michael, *Ber.*, 1877, **10**, 1554, quote 114—115°).

*Menthyl acetophenone-o-carboxylate* was prepared from the above acid by esterification in the presence of dry hydrogen chloride. The crude ester was freed from most of the excess menthol by heating at  $200^{\circ}$  under 10 mm. pressure, and was recrystallised from light petroleum until of constant rotation. The pure compound separated in colourless, odourless crystals, m. p.  $92^{\circ}$  (Found: C, 75.4; H, 8.6.  $C_{19}H_{26}O_3$  requires C, 75.5; H, 8.6%).

The compound dissolves comparatively readily in benzene, but is not very soluble in other organic solvents at the ordinary temperature.

The following figures refer to the rotatory power of the ester in the fused state at  $94^{\circ}$ . All rotations were measured in a 50 mm. tube and were negative in sign.  $D_4^{94} = 0.9898$  ( $\alpha_{vi}$  could not be determined owing to the slight yellow tint of the liquid).

$\alpha_D$ .	$\alpha_{Fe}$ .	$\alpha_{Gr}$ .	$\alpha_{Gr}/\alpha_D$ .	$[\alpha]_D$ .	$[\alpha]_{Fe}$ .	$[\alpha]_{Gr}$ .	$[M]_D$ .
42.84	45.04	51.98	1.213	86.56	91.01	105.0	261.4

In addition, a number of measurements were made of the rotatory power in solution at about  $20^{\circ}$ . In each case the highest concentration quoted represents the maximum at which it is convenient to work, and is not far removed from the saturation point. All rotations are negative in sign.

Solvent.	G. of ester in 100 c.c.	$\alpha$ obs.	( $l = 2$ ).	$[\alpha]_D$ .	$\alpha_{Gr}/\alpha_D$ .	$[M]_D$ .
Benzene ( $20^{\circ}$ ).	5.000	$\alpha_D$	9.42	94.2	1.216	284.5
		$\alpha_{Fe}$	9.90	99.0		
		$\alpha_{Gr}$	11.46	114.6		
		$\alpha_{vi}$	22.03	220.3		
		$\alpha_D$	37.68	94.15		
Benzene ( $20.1^{\circ}$ ).	20.010	$\alpha_{Gr}$	45.60	113.9	1.211	284.3
		$\alpha_D$	37.68	94.15		
Acetone ( $18.8^{\circ}$ ).	5.054	$\alpha_D$	8.48	83.9	1.211	253.4
		$\alpha_{Fe}$	8.90	88.1		
		$\alpha_{Gr}$	10.26	101.5		
		$\alpha_{vi}$	18.85	186.5		
Alcohol ( $19.5^{\circ}$ ).	2.001	$\alpha_D$	3.54	88.46		267.0
		$\alpha_{Gr}$	18.85	186.5		

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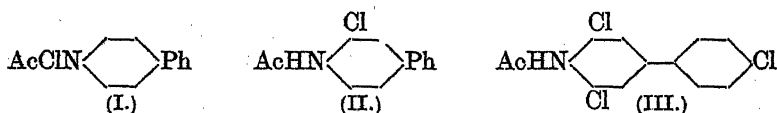
LXXVI.—*The Chlorination and Bromination of 4-Aminodiphenyl.*

By HAROLD ARCHIBALD SCARBOROUGH and WILLIAM ALEXANDER WATERS.

THE action of chlorine or bromine on 4-aminodiphenyl and on its acetyl derivative appears to have been investigated in only one instance, where it was shown that, by direct bromination of 4-acetylaminodiphenyl, 4'-bromo-4-acetylaminodiphenyl resulted (Hübner, *Annalen*, 1881, 209, 339). Other halogen derivatives, however, have been prepared from benzidine and from tolidine by an adaptation of the Sandmeyer reaction (Taüber, *Ber.*, 1894, 27, 2627; Gelmo, *Ber.*, 1906, 39, 4175); the structure of these compounds necessarily follows from their method of preparation.

The present investigation had as its objects the preparation of the *N*-halogen derivatives and their conversion into ring-substituted products; and the direct introduction of chlorine or bromine into the molecule of 4-aminodiphenyl or 4-acetylaminodiphenyl.

It was found that a stable *N*-chloro-4-acetylaminodiphenyl (I) could be obtained from which 3-chloro-4-acetylaminodiphenyl (II) resulted; the latter compound again could be converted into a *N*-chloro-derivative which was unstable, lost chlorine, and from which a ring-substituted product could not be obtained. The corresponding *N*-bromo-4-acetylaminodiphenyl could be prepared only in an impure state, it lost bromine with ease, and the original acetyl derivative was not recovered.



The chlorination of the free base was attempted under various conditions, but only deeply coloured and tarry products were obtained. In contrast to this, the acetylated base could be substituted readily with the formation of 3-chloro-4-acetylaminodiphenyl, and on further chlorination 3:5:4'-trichloro-4-acetylaminodiphenyl (III) was obtained. It was found impossible to introduce more than these three atoms of chlorine into the molecule and obtain a product capable of being separated into individual compounds.

The bromination of the free base proceeded smoothly, yielding 3:5-dibromo-4-aminodiphenyl, and under altered conditions the latter compound could be further brominated to give 3:5:4'-tribromo-4-aminodiphenyl. Higher bromination products appear

to be formed; but from the mixture of substances produced it has been found impossible, so far, to isolate individual compounds. The acetyl derivative of the base on bromination yielded either 4'-bromo-4-aminodiphenyl or its acetyl derivative and a small quantity of a dibrominated product which has been shown to be 3:4'-dibromo-4-acetylaminodiphenyl. Bromination at a higher temperature yielded 3:5:4'-tribromo-4-aminodiphenyl.

The orientation of substituents in the nuclei of diphenyl is of a complex nature; thus whilst 4-aminodiphenyl and its acetyl derivative on chlorination or nitration yield a product substituted in the position adjacent to the amino-group, yet when the substituent in the 4-position is varied as widely as the halogens, the nitro-group and the carboxyl group the entering substituent goes to the 4'-position.

As the direct substitution of only 2- and 4-monosubstituted diphenyl derivatives has been investigated, it is impossible to put forward more than tentative suggestions. The following assumptions appear to be necessary :

(a) The usual directive influence is to be ascribed to all the simple groups.

(b) The phenyl group and the group  $C_6H_4X$  (where X may be an ortho-para or meta-directing group) have a strong ortho-para-directive influence.

(c) The amino-, hydroxy-, and derived groups promote substitution in the same nucleus.

Thus it appears that the position taken up by a substituent depends on the velocity with which substitution can be effected. This is in agreement with the experimental evidence that ortho-para-directing groups, and in particular the amino- or hydroxy-group, render substitution easy, whereas meta-directing groups tend to make substitution a comparatively slow process.

Alternatively, it might be suggested that substitution only occurs in the nucleus containing the directing group when this group is capable of being itself substituted and then undergoing a rearrangement which transfers the substituent to the ring. This would be in accord with the behaviour of amino- and hydroxy-groups.

The behaviour of 4-acetylaminodiphenyl on monobromination is very striking, since it appears to be the only known case among the substitution products of 4-amino- or 4-hydroxy-diphenyl in which the first substituent enters the 4'-position; this result is still more unexpected, since 4-aminodiphenyl itself gives rise to a normal sequence of substitution products.

This abnormal behaviour might be ascribed to (a) a mechanism for this bromination different from that involved in all other cases, or (b) steric influences. Three alternative mechanisms appear

possible: (1) the formation of a *N*-halogen compound followed by an *intramolecular* change; (2) the formation of a *N*-halogen compound followed by an *intermolecular* change; and (3) the direct interaction of the halogen and the aminodiphenyl molecules. Since *N*-bromo-4-acetylaminodiphenyl cannot be converted into a ring-substituted product, mechanism (1) cannot be the mechanism involved; since the corresponding *N*-chloro-compound can be thus transformed and since direct chlorination yields the same product, any one of the three mechanisms may be involved.

To ascribe the difference in behaviour to a steric factor would imply that by acetylation of the base the velocity of interaction of bromine with the more reactive hydrogen atoms in the 3- and 5-positions is decreased to such an extent that the less reactive hydrogen atom in the 4'-position is substituted almost exclusively.

It is the intention of the authors to complete a study of the chlorination and bromination of 2-aminodiphenyl and to extend the work to a consideration of 3-nitro- and 3-amino-diphenyl.

#### EXPERIMENTAL.

4-Aminodiphenyl was prepared by nitrating diphenyl by Ludens's method (*Ber.*, 1875, 8, 871) and reducing the product by Schlenk's method (*Annalen*, 1909, 368, 303).

*N*-Chloro-4-acetylaminodiphenyl.—To a suspension of 10.6 g. of 4-acetylaminodiphenyl in a solution of 13 g. of sodium bicarbonate in 200 c.c. of water, 150 c.c. of *N*-sodium hypochlorite were added during 2 hours. The product was collected after 12 hours, washed with water, dried, and extracted with light petroleum (b. p. 40–60°), in which 4-acetylaminodiphenyl is insoluble. The *chloroamine* crystallised from carbon tetrachloride in colourless needles, m. p. 129.5° (Found: Cl, 14.3.  $C_{14}H_{12}ONCl$  requires Cl, 14.4%).

3-Chloro-4-acetylaminodiphenyl.—(a) *Conversion of the chloroamine.* To a hot solution of 5 g. of the chloroamine in 100 c.c. of spirit and 2–3 c.c. of glacial acetic acid, sufficient water was added to start precipitation. The product separated on cooling, and crystallised from dilute alcohol in needles, m. p. 147°.

(b) *Direct chlorination of 4-acetylaminodiphenyl.* Chlorine was passed into a 2% solution of the acetylamine in glacial acetic acid, cooled in ice-water, until the theoretical gain in weight was obtained. The product, which was precipitated with water, contained higher chlorination products (Found: Cl, 14.7.  $C_{14}H_{12}ONCl$  requires Cl, 14.4%).

3-Chloro-4-aminodiphenyl hydrochloride was obtained on hydrolysis of the acetyl derivative with 10% alcoholic hydrochloric acid. The

salt separated from the solution, on cooling, in long needles, m. p.  $217^{\circ}$  (decomp.) (Found: HCl, 15.1.  $C_{12}H_{10}NCl$ , HCl requires HCl, 15.2%).

3-Chloro-4-aminodiphenyl was precipitated from the solution of the hydrochloride by dilute ammonia. It crystallised from dilute alcohol in needles, m. p.  $71^{\circ}$  (Found: Cl, 17.2.  $C_{12}H_{10}NCl$  requires Cl, 17.4%).

3:4-Dichlorodiphenyl, obtained from the amine by the usual methods, was a faintly yellow oil, b. p.  $195-200^{\circ}/15$  mm., which solidified to a pale yellow, crystalline mass, m. p.  $46^{\circ}$  (Found: Cl, 30.8.  $C_{12}H_8Cl_2$  requires Cl, 31.8%). On oxidation of this crude product with chromic anhydride in glacial acetic acid solution, 3:4-dichlorobenzoic acid was obtained (m. p.  $200^{\circ}$ ).

3-Chloro-4-acetylchloroaminodiphenyl.—The chloroamine was prepared in the manner described for 4-acetylchloroaminodiphenyl. It was a white powder soluble in non-aqueous solvents; it could not be obtained pure owing to the ease with which it lost chlorine. Several attempts were made, under various conditions, to bring about a rearrangement, but in each case chlorine was evolved and 3-chloro-4-acetylaminodiphenyl was obtained.

3:5:4'-Trichloro-4-acetylaminodiphenyl.—Chlorine and carbon dioxide were passed slowly into a 5% solution of 4-acetylaminodiphenyl, the temperature being kept as low as possible. Excess chlorine was removed with a current of air, and the solution diluted with water until precipitation commenced. The product crystallised from acetone in needles, m. p.  $236^{\circ}$  (Found: Cl, 33.6.  $C_{14}H_{10}ONCl_3$  requires Cl, 33.8%).

3:5:4'-Trichloro-4-aminodiphenyl.—The acetyl derivative was hydrolysed with alcoholic hydrochloric acid; the amine, which separated from the solution in long needles, was recrystallised from alcohol; m. p.  $128^{\circ}$  (Found: Cl, 38.9.  $C_{12}H_8NCl_3$  requires Cl, 39.05%). On oxidation with chromic anhydride in glacial acetic acid solution, *p*-chlorobenzoic acid was obtained (m. p.  $235^{\circ}$ ).

*N*-Bromo-4-acetylaminodiphenyl was obtained as was the corresponding chloro-compound. It was a pale yellow powder, easily soluble in non-aqueous solvents, and lost bromine very easily. As it could not be obtained pure, it was not further investigated.

4'-Bromo-4-aminodiphenyl.—To a well-cooled 10% solution of 4-acetylaminodiphenyl in glacial acetic acid was added slightly more than 1 mol. of bromine. After 24 hours, on pouring into water, a mixture of brominated products was obtained which, by fractional crystallisation from dilute acetic acid, was separated into a more soluble monobromo-derivative and a less easily soluble dibromo-derivative. The former was 4'-bromo-4-aminodiphenyl and not its

acetyl derivative (compare Hübner, *loc. cit.*). It crystallised from dilute acetic acid in long needles, m. p.  $145^{\circ}$  (Found: Br, 32.2.  $C_{12}H_{10}NBr$  requires Br, 32.1%). On oxidation with chromic anhydride in glacial acetic acid solution, *p*-bromobenzoic acid was obtained (m. p.  $251^{\circ}$ ).

3 : 4'-Dibromo-4-acetylaminodiphenyl.—The less soluble dibromo-derivative crystallised from acetone in colourless needles, m. p.  $197^{\circ}$  (Found: Br, 43.25.  $C_{14}H_{11}ONBr_2$  requires Br, 43.4%). The acetyl derivative was hydrolysed with alcoholic hydrobromic acid. The free base was not purified and analysed, as only a very small quantity was available; but was converted directly into a tribromo-derivative by bromination in glacial acetic acid solution. The product was crystallised from acetone and then from dilute acetic acid; it had m. p.  $148^{\circ}$ , alone or mixed with 3 : 5 : 4'-tribromo-4-aminodiphenyl. The original acetyl derivative was not identical with 3 : 5-dibromo-4-acetylaminodiphenyl, whence it follows that the acetyl derivative must have the bromine atoms in the 3- and 4'-positions.

3 : 5-Dibromo-4-aminodiphenyl.—The calculated quantity of a 10% solution of bromine in glacial acetic acid was added to a cold glacial acetic acid solution of 4-aminodiphenyl. The yellow precipitate was filtered off and washed with dilute sodium carbonate solution. It crystallised from alcohol in colourless needles, m. p.  $119^{\circ}$  (Found: C, 44.1; H, 2.9; Br, 48.8.  $C_{12}H_9NBr_2$  requires C, 44.05; H, 2.8; Br, 48.9%).

3 : 5-Dibromo-4-acetylaminodiphenyl was prepared by heating the base with acetic anhydride in glacial acetic acid solution. After crystallising from alcohol, it melted at  $162^{\circ}$  (Found: Br, 43.45.  $C_{14}H_{11}ONBr_2$  requires Br, 43.4%).

3 : 5-Dibromodiphenyl, obtained from the base by elimination of the amino-group in the usual manner, was a pale yellow oil, b. p.  $208^{\circ}/15$  mm., m. p.  $15^{\circ}$  (Found: Br, 51.3.  $C_{12}H_8Br_2$  requires Br, 51.3%). On oxidation with chromic anhydride in glacial acetic acid solution in a sealed tube at  $200^{\circ}$  3 : 5-dibromobenzoic acid was obtained (m. p.  $212^{\circ}$ ).

3 : 5 : 4'-Tribromo-4-aminodiphenyl.—Bromine (1 mol.) was added to a boiling solution of 3 : 5-dibromo-4-aminodiphenyl in glacial acetic acid, and the mixture refluxed until the colour of the bromine had disappeared (usually about 45 minutes). The product precipitated by addition of water crystallised from dilute acetone in white needles, m. p.  $149^{\circ}$ . The same substance was obtained by direct bromination of 4-acetylaminodiphenyl in boiling glacial acetic acid (Found: C, 35.4; H, 2.0; Br, 59.0.  $C_{12}H_8NBr_3$  requires C, 35.4; H, 2.2; Br, 59.0%). On oxidation with chromic anhydride

in glacial acetic acid solution *p*-bromobenzoic acid was obtained (m. p. 251°).

The *acetyl* derivative crystallised from acetone in white needles, m. p. 256° (Found: Br, 53.5.  $C_{14}H_{10}ONBr_3$  requires Br, 53.6%).

All m. p.'s recorded in this paper have been corrected, and where necessary the identity of a substituted benzoic acid was established by the "mixed m. p." method.

The authors wish to express their thanks to Dr. H. McCombie for the interest he has taken in the work. One of them (W. A. W.) is indebted to the Master and Fellows of Gonville and Caius College for a studentship which enabled him to collaborate in this work.

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### LXXVII.—*The Influence of the Intensity of Illumination on the Velocity of Photochemical Changes. The Determination of the Mean Life of a Hypothetical Catalyst.*

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ERNEST WALTERS.

ONLY a few researches have been conducted on the variation of the rates of photochemical changes with the intensity of the light, and at present there is some degree of discordance in the conclusions drawn by different experimenters from the results of their experiments.

Draper (*Phil. Mag.*, 1843, 23, 401) announced that the rate at which chlorine and hydrogen combine in light is proportional to the intensity of the illumination. Baly and Barker (*J.*, 1921, 119, 653) maintained that the ratio of the rate of union of the two gases to the intensity of the light increases as the intensity of the light is increased. M. C. C. Chapman (*J.*, 1924, 125, 1521) obtained a result in substantial agreement with that of Draper. She found, however, that as the intensity of the radiation is increased the rate of formation of hydrochloric acid increases in a slightly smaller ratio. Berthoud (*Helv. Chim. Acta*, 1924, 7, 324) considered that the rate of union of chlorine and hydrogen in the absence of inhibitors would be proportional to the square root of the intensity of illumination, and he saw in some of Mrs. Chapman's results evidence that such is the case. Kornfeld and Müller (private communication from Professor Bodenstein) have confirmed Mrs. Chapman's results. They find



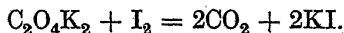
that the rate of formation of hydrochloric acid is proportional to the intensity of the light when the intensity is varied in the ratio of 1 : 64.

Draper, Baly and Barker, and Mrs. Chapman used electrolytic gas, which always contains a small amount of oxygen. Kornfeld and Müller removed oxygen from the hydrogen; but the chlorine they used may have contained a little oxygen.

It is possible that Berthoud's contention is right. The electrolytic gas used by Mrs. Chapman undoubtedly contained a little oxygen, and the small deviations from proportionality observed by her were in the direction required by Berthoud's view.

In a recent paper by Bodenstein and Lütkemeyer (*Z. physikal. Chem.*, 1924, **114**, 208) on the photochemical synthesis of hydrobromic acid it is concluded that the rate of formation of this compound from its elements is directly proportional to the square root of the intensity of the light. The striking difference, in this particular, of the influence of light on mixtures of bromine with hydrogen and of chlorine with hydrogen may possibly be due to the effect of small quantities of oxygen on the photochemical union of the latter gases. The question needs to be submitted to further investigation.

In connexion with the subject of this communication, the reaction between iodine and potassium oxalate is of especial interest. This reaction is represented by the equation :



It has been studied by Dhar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **16**, 1097; *Ann. Chim.*, 1919, **11**, 130; *J.*, 1923, **123**, 1856) and by Berthoud and Bellenot (*Helv. Chim. Acta*, 1924, **7**, 307). In his first paper, Dhar maintained that the velocity of the action is proportional to the intensity of the light. On the other hand, Berthoud and Bellenot asserted that it is proportional to the square root of the intensity of the light, both for red and for blue light. In order to vary the intensity of the light the latter investigators inserted between the source of illumination and the solution a large disc of black cardboard which could be set in rapid rotation, and from which two equal sectors had been removed for the first series of measurements; four for a second series, and eight for a third series, so as to make the intensity vary in the ratios 1 : 2 : 4. They realised that this method of varying the intensity of the light would not be legitimate unless the duration of the secondary reactions considerably exceeded the intervals between successive illuminations, and they deduced that if this condition were fulfilled the velocity of reaction ought to diminish as the rate of rotation of

the disc is reduced. They observed the anticipated falling off in the velocity of the reaction, but they were unable to obtain the theoretical result when the disc was rotating very slowly.

We have repeated the experiments of Dhar and of Berthoud and Bellenot, and our results agree with those of the latter researchers. We have also examined more closely the theory of the effect of intermittent illumination on photochemical reactions of the same class, and have drawn conclusions from the theory and from our experimental results which will be given below.

The reaction between potassium oxalate and iodine, according to Berthoud and Bellenot, is of the same class as that between chlorine and hydrogen. One quantum of absorbed light is sufficient to cause the interaction of a large number of molecules of the reacting substances. For the explanation of such reactions several special hypotheses have been proposed. These hypotheses have one feature in common in that they postulate the formation of an unstable catalyst (or chain of catalysts) by the direct action of the light. We shall make no special assumption concerning the nature of the catalyst, but we shall assume that :

(I) the rate of formation of the catalyst is proportional to the intensity of illumination;

(II) the rate of reaction is proportional to the concentration of the catalyst; and

(III) the rate of destruction of the catalyst is proportional to a power of its concentration.

If  $[A]$  represents the concentration of the catalyst and  $I$  the intensity of the light, we have from assumptions I and III

$$\begin{aligned} d[A]/dt &= cI - k[A]^n \\ &= 0 \text{ in the steady state,} \end{aligned}$$

and therefore in the steady state

$$I^{1/n} \propto [A] \propto \text{the rate of reaction (from assumption II).}$$

Therefore in the case of the formation of hydrochloric acid from electrolytic gas  $n = 1$  if the experiments of Mrs. Chapman and of G. Kornfeld and H. Müller are trustworthy, whereas in the case of the interaction of iodine and potassium oxalate  $n = 2$  if the observations of Berthoud and Bellenot and of the authors are not subject to some unsuspected source of error.

We have spent 6 months in attempts to discover some explanation of Berthoud and Bellenot's results other than that given by the authors, namely, that in this reaction the velocity of change is not proportional to the intensity of illumination but to its square

root, and we have satisfied ourselves that none of the following causes could furnish such an explanation :

- (1) The presence of an inhibitor.
- (2) The varying rates of escape of the carbon dioxide produced in the reaction.
- (3) The more rapid removal of the iodine from that portion of the solution which is nearest to the light.
- (4) The method employed for varying the intensity of the light.\*

When the method of varying the intensity of the light was that of a rotating disc, consistent and reproducible results in agreement with those of Berthoud and Bellenot were obtained. The results were independent of the rate of rotation of the disc when this rate exceeded one thousand revolutions per minute. It must therefore be concluded that when the solution has been exposed to light the chemical action continues for some time after the light has been shut off: for otherwise the rate of chemical change would be

\* That inhibitors were not present was proved by the fact that the velocity of the reaction was not affected by the purification of the materials used (*i.e.*, by the fractional crystallisation of the potassium oxalate or by the sublimation of the iodine), the results being reproducible and, within reasonable limits, independent of the degree of purity of the reagents. Variation of the hydrogen-ion concentration had very little effect.

That the dissolved carbon dioxide had no effect was proved by the fact that the total amount of change in a given time, employing a constant intensity of light, was the same when the exposure was continuous and when it was intermittent, provided that the intervals of exposure were not too short.

Another method employed for varying the intensity of the light was the following. Two one thousand-watt lamps, A and B, were placed side by side so as to be symmetrically situated with respect to the reaction tube, which was contained in a thermostat. The currents passed through the lamps were separately adjusted so that each lamp emitted light of the same intensity. The reaction vessel was exposed for 4 hours to the light emitted by A alone, and then for 4 hours to the light emitted by B alone. The change was measured, and compared with that effected in half the time by an exposure of the reaction vessel, filled with a solution of the same composition, to the light emitted simultaneously by both lamps. The mean ratio of the change effected by the light from one lamp in 8 hours to that effected by the light from two lamps in 4 hours was 1.32 : 1, the theoretical result calculated on the assumption that the rate of change is proportional to the square root of the intensity of the light being 1.41 : 1. The fact that the theoretical ratio was greater than that found experimentally can be explained by the circumstance that the large size of the bulbs of the two lamps made it impossible to place their filaments close together. That the effect of this source of error would be in the direction stated can be seen immediately by considering the effect of placing the lamps on opposite sides of the comparatively strongly absorptive solution.

proportional to the number of sectors left open in the disc, and not to the square root of this number. In other words, the catalyst assumed above has a life of appreciable duration.

*Determination of the Life of the Catalyst or Chain.*—The rate of disappearance of the catalyst is given by  $k[A]^2$  and therefore in the steady state the mean life of the catalyst is

$$[A]/k[A]^2 = 1/k[A].$$

The problem is therefore to determine the value of  $k[A]$  when the solution is exposed to light of a given intensity and has reached the steady state.

In the light

$$d[A]/dt = cI - k[A]^2.$$

Multiply both sides of the equation by  $k$  and put  $ckI = a^2$  and  $k[A] = x$ .

The equation becomes

$$dx/dt = a^2 - x^2.$$

Or putting  $\tau$  for  $at$ , and  $y$  for  $x/a$ ,

$$dy/d\tau = 1 - y^2$$

the solution of which is

$$\frac{y_2}{y_1} \left[ \log_e \frac{1+y}{1-y} \right] = 2\tau_2 - 2\tau_1 \quad . \quad . \quad . \quad (1)$$

$y$  is the ratio of  $k[A]$  at the moment under consideration to its value in the steady state when the intensity of the light is  $I$ , and  $\tau$  is the ratio of the time,  $t$ , to the duration of a mean life.

The differential equation which holds in the dark is

$$d[A]/dt = -k[A]^2$$

and its solution in terms of the variable  $y$  and  $\tau$  is

$$\frac{1}{y_3} - \frac{1}{y_2} = \tau_3 - \tau_2 \quad . \quad . \quad . \quad (2)$$

in which  $y_3$  and  $y_2$  are the final and initial values of  $y$ , and  $\tau_3$  and  $\tau_2$  the corresponding values of  $\tau$ .

In our experiments, the disc has eight sectors, each of angle  $\pi/8$ , symmetrically situated. Accordingly, when the disc was rotating uniformly, the duration of illumination was equal to the time during which the light was shut off, i.e.,  $\tau_2 - \tau_1 = \tau_3 - \tau_2$ . Also under the same conditions  $y_1$  must attain a steady value which must be equal to  $y_3$ . Therefore from (1) and (2)

$$\log_e \frac{1+y_2}{1-y_2} + \frac{2}{y_2} = \log_e \frac{1+y_1}{1-y_1} + \frac{2}{y_1}.$$

For each value of  $y_1$  the corresponding value of  $y_2$  can be obtained from the above equation.

Moreover, if the value of  $\tau$  is selected such that when  $y = 0$   $\tau = 0$ , equation (1) becomes

$$\log_e \frac{1+y}{1-y} = 2\tau \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for each value of  $y$  there is a corresponding value of  $\tau$ .

We shall now find the mean value of  $y$  for a given rate of rotation of the disc. From (3) the value of  $y$  during illumination is given by

$$y = \tanh \tau$$

and from (2) the value of  $y$  during the period of non-illumination is given by

$$y = 1 / \left( \tau + \frac{1}{y_2} \right)$$

in which  $\tau$  is the time (taking the mean life as the unit) during which the solution is in the dark and  $y_2$  is the value of  $y$  when the light is shut off.

The mean value of  $y$  during uniform rotation of the disc is manifestly given by

$$y = \frac{\log_e \cosh \tau_2 - \log_e \cosh \tau_1 + \log [(\tau_2 - \tau_1)y_2 + 1]}{2(\tau_2 - \tau_1)}$$

But the mean value of  $y$  when the disc is rotating very rapidly is  $1/\sqrt{2}$ . Consequently, since the mean value of  $y$  is proportional to the rate of chemical change,

$$\frac{\log_e \cosh \tau_2 - \log_e \cosh \tau_1 + \log [(\tau_2 - \tau_1)y_2 + 1]}{\sqrt{2}(\tau_2 - \tau_1)} = \frac{\text{rate of change when the disc rotates at the given rate}}{\text{rate of change when the disc rotates very rapidly}}$$

By trial a value of  $\tau_1$  is found which satisfies this equation. This can be done, since for every value of  $\tau_1$  there are corresponding values of  $\tau_2$  and  $y_2$ . Furthermore, as  $\tau_2 - \tau_1$  is the duration of the exposure to light in mean lives, the value of the mean life can be calculated from the known rate of rotation of the disc.

#### EXPERIMENTAL.

The composition of the solution was potassium oxalate  $N/2$ , iodine  $0.00625N$ , and potassium iodide  $0.00931N$ . The reaction vessel was a glass cylinder of 4 cm. diameter, and it contained 80 c.c. of the above solution. The cylinder was closed with a ground glass stopper in order to prevent loss of iodine by evaporation, and during an experiment it was maintained at a temperature of  $20^\circ$

in a thermostat filled with water and having sides of plane glass. A black screen was placed behind the reaction tube and the thermostat was covered so that no light could enter it except that which had passed through a sector of the disc and a window of the same shape as the sector in one of the glass sides of the thermostat. The reaction tube was placed near to the window in such a position that the whole of the solution it contained was equally illuminated. The source of light was a thousand-watt incandescent lamp placed at a horizontal distance of 38 cm. from the reaction vessel. The light from the lamp passed through an aperture of an appropriate shape in a large piece of cardboard which was placed immediately in front of the lamp, the aperture being of such a size that its penumbra was outside the window of the thermostat. The rotating disc was as near as possible to the thermostat and the reaction vessel. The shadow cast by the edge of the sector was quite sharp, but there was some error which could neither be avoided nor estimated, occasioned by reflexion from the inner wall of the glass bulb of the lamp. The lamp itself was, of course, placed in such a position that its incandescent wire subtended in a plane at right angles to the top edge of the window the minimum angle at a point in the solution. The disc was kept in rotation by means of a geared motor, and in some of the experiments in which the rotation was slow by a clock. The rates of chemical change were determined by finding the times required to bring about the same amount of chemical change as estimated by titration of the iodine with a standard solution of sodium thiosulphate. The mean life of the catalyst was in the first place determined when the solution was illuminated with white light. The results are recorded below :

A.	B.	C.	D.
20	71.75		
20	71.44		
Very fast	62.21	0.0303	0.000688
"	62.20		
24	71.12		
24	70.68	0.0299	0.000678
Very fast	62.21		

In column A is recorded the number of revolutions per minute of the disc; in column B the time of exposure in minutes needed to effect the same amount of chemical change; in column C the calculated mean life, in seconds; and in column D the quotient of the mean life and the time required to effect the given amount of chemical change when the solution was exposed without interruption to the light. This quotient should be a constant.

In a third determination light which had been filtered through a solution of iodine was used. The light passed through 5.5 cm. of an aqueous solution of iodine and potassium iodide of such a

strength that the concentration of each of the dissolved substances was twice as great as the corresponding concentration in the solution contained in the reaction vessel. The effect of using such filtered light would, of course, be to render the velocity of chemical change much more uniform throughout the solution. The results are recorded below :

A.	B.	C.	D.
21	293.2		
5	327.8		
5	324.7		
Very fast	282.8	0.1212	0.000605

From any of the above results the mean life of the catalyst in the dark at the temperature of the experiment can be calculated, provided that the rate of the chemical change in the dark is known, and similar assumptions are made concerning the mechanism of the change. The time required to effect the specified amount of change in the dark was found by experiment to be 10,430 minutes. Using the constant determined in the last experiment, we have the mean life of the catalyst in the dark =  $10430 \times 0.000605 = 6.31$  seconds.

Although we are unable without conducting further research to estimate the errors of the methods described for determining the constant, we believe that the accuracy of the determination is sufficient for present needs, namely, for the purpose of testing a hypothesis.

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## LXXVIII.—*The Action of Alkaline Arsenites on Some Halogenated Organic Compounds.*

By ISIDORE ELKANAH BALABAN.

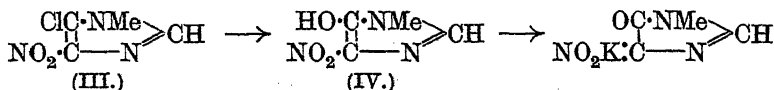
It is well known that sulphonic acids, both aliphatic and aromatic, may be obtained by the action of alkali sulphites on some halogenated organic compounds. In view of the chemotherapeutic importance of arsinic acids, it was thought worth while to investigate the action of alkali arsenites on a series of halogenated organic compounds of varying degrees of reactivity, in order, if possible, to delimit the applicability of the method. Meyer (*Ber.*, 1883, 16, 1440) first employed the method to prepare methyl- and ethyl-arsinic acids, and it was extended to *n*-propyl-, isoamyl-, and benzyl-arsinic acids by Dehn and McGrath (*J. Amer. Chem. Soc.*, 1906, 28, 351). Quick and Adams (*ibid.*, 1922, 44, 809) applied it successfully

to butyl bromide and allyl bromide, whilst Palmer (*ibid.*, 1923, 45, 3023) applied it to chloroacetic acid. In the aromatic series, Rosenmund (*Ber.*, 1921, 54, 438) obtained *o*-benzarsinic acid by the action of potassium arsenite on *o*-bromobenzoic acid.

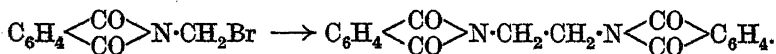
Two glyoxaline derivatives have now been examined containing highly reactive halogen atoms, 4(5)-methyl-5(4)-chloromethylglyoxaline (I) and 5-chloro-1-methyl-2-chloromethylglyoxaline (II), but only the corresponding alcohols could be isolated in poor yield.



A less reactive glyoxaline compound, 5-chloro-4-nitro-1-methylglyoxaline (III), which had previously been shown to give a sulphonic acid (Balaban and Pyman, J., 1924, 125, 1564), when heated with potassium arsenite in absolute alcohol gave 4-nitro-5-hydroxy-1-methylglyoxaline (IV), a very unstable nitroamide resembling in general properties the nitroacetone and nitroacetophenone of Lucas (*Ber.*, 1899, 32, 600) and Henry (*ibid.*, 1899, 32, 865).



The nitroamide is, however, stable as its *potassium* and *sodium* salts. 2:4-Dinitrobenzene, which resembles the foregoing in containing a halogen atom activated by a nitro-group, yielded 2:4-dinitrophenol, whereas by the action of sodium sulphite in aqueous alcoholic solution it is known to yield 1:3-dinitrobenzene-4-sulphonic acid (D.R.-P. 65240). When 8-chlorocaffeine is heated with potassium arsenite in alcohol at 140–180°, a mixture of 8-hydroxy- and 8-ethoxy-caffeine is obtained. Under somewhat parallel conditions (D.R.-P. 74045), 8-chlorocaffeine is known to yield a sulphonic acid when treated with aqueous sodium sulphite. In the foregoing cases where reaction had taken place, the halogen atom was replaced by hydroxyl or ethoxyl. An unexpected result was, however, obtained on examining the action of alkali arsenite on phthalbromomethylimide in acetone solution, as ethylenediphthalimide was isolated.



When it was boiled with 20% aqueous sodium sulphite, *phthalimido-methanesulphonic acid* was obtained in a yield of 13.2% of the theoretical, the main product being phthalic acid (yield 62%), together with a small amount of phthalimide. An attempt to hydrolyse the sulphonic acid to the unknown aminomethanesulphonic



acid proved unsuccessful. Delépine and Demars also failed to obtain this compound by the action of ammonia on chloromethane-sulphonic acid (*Bull. Soc. Pharmacol.*, 1922, 29, 14).

In none of the above cases, although special search was made, was any organic arsenic acid found. If this result be contrasted with the much more general formation of sulphonic acids by the action of alkali sulphite, one is compelled to attribute it to the difference in alkalinity of sulphite and arsenite.

#### EXPERIMENTAL.

The action of alkali arsenites was examined on the following halogenated organic compounds: 4(5)-*Methyl-5(4)-chloromethylglyoxaline* (I). To a mechanically stirred solution of potassium arsenite (24 g.; 10 mols.) in water (30 c.c.) below 0°, 4(5)-methyl-5(4)-chloromethylglyoxaline hydrochloride (2 g.) in absolute alcohol (50 c.c.) was run in during  $\frac{1}{2}$  hour. After removal of much arsenic trioxide the mother-liquor was evaporated to dryness in a vacuum, the residue extracted with absolute alcohol, and the extract added to aqueous picric acid; 4(5)-methyl-5(4)-hydroxymethylglyoxaline picrate (1.1 g.; yield, 27.5%) was the sole product obtained. It melted at 180°, alone or mixed with an authentic specimen.

The experiment was repeated in absolute alcohol, but no definite organic products could be isolated.

5-*Chloro-1-methyl-2-chloromethylglyoxaline* (II), treated as in the above two experiments, yielded 5-chloro-1-methyl-2-hydroxymethylglyoxaline picrate (3 g.; yield, 64%), m. p. 148–149°, and 0.8 g., m. p. 148°, respectively, but no trace of other organic material.

5-*Chloro-4-nitro-1-methylglyoxaline* (III). The nitro-compound (2 g.) was boiled under reflux with potassium arsenite (5 g.) in absolute alcohol (50 c.c.) for 8 hours, together with a crystal of potassium iodide. On keeping, clusters of yellow needles crystallised (4.2 g.). This product was extracted with water (20 c.c.), and after removal of arsenic trioxide the filtrate was acidified (Congo-paper); 1.07 g. of solid crystallising in fine, colourless needles and decomposing at 106° were then obtained.

4-*Nitro-5-hydroxy-1-methylglyoxaline* (IV) is soluble in water, alcohol, dilute acids and alkalis, and the usual organic solvents. It cannot be recrystallised, as the solution rapidly becomes dark red, and acquires a strong odour of oxides of nitrogen. It was unsuitable for combustion, as it decomposed very rapidly. In alcoholic solution, the nitroamide gives with ferric chloride an intense brown coloration. It also gives the Liebermann nitroso-reaction. The *potassium* salt, prepared by carefully neutralising the nitro-amide

with dilute potassium hydroxide and evaporating the solution to dryness over sulphuric acid, crystallised in fine, long, yellow needles, decomp.  $292^{\circ}$ , containing  $\frac{1}{2}\text{H}_2\text{O}$ , which was very gradually lost at  $95^{\circ}$  (Found in air-dried substance:  $\text{H}_2\text{O}$ , 4.7; K, 20.4, 20.6.  $\text{C}_4\text{H}_4\text{O}_3\text{N}_3\text{K}, \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 4.7; K, 20.5%). The sodium salt, obtained in a similar manner, crystallised in minute, yellow, anhydrous prisms, decomp.  $320^{\circ}$  (Found: Na, 13.6.  $\text{C}_4\text{H}_4\text{O}_3\text{N}_3\text{Na}$  requires Na, 13.9%).

**2 : 4-Dinitrobromobenzene.** The nitro-compound (2.5 g.), potassium arsenite (8 g.), and absolute alcohol (50 c.c.) were heated under reflux on the water-bath for 8 hours. The product having been worked up as in the previous experiments, 2 : 4-dinitrophenol (1 g.), m. p.  $113-114^{\circ}$ , alone or mixed with an authentic specimen, was isolated. A further crop (0.5 g.), m. p.  $110^{\circ}$ , was also obtained.

**8-Chlorocaffeine.** Potassium arsenite (5 g.), 8-chlorocaffeine (2.3 g.), and absolute alcohol (50 c.c.) were similarly heated for 7 hours. The alcoholic mother-liquor gave 0.75 g., m. p.  $160^{\circ}$ , which after recrystallisation proved to be unchanged material; no products were isolated. The experiment was repeated in aqueous solution, ammonia or methylamine being evolved. After keeping, 0.85 g. of a substance, m. p.  $186^{\circ}$  alone or mixed with 8-chlorocaffeine, was collected, no other organic matter being obtained. A third experiment was carried out with absolute alcohol in a sealed tube at  $140-180^{\circ}$  for 8 hours. The alcohol-insoluble portion (0.4 g.) was hydroxycaffeine (m. p. ca.  $335^{\circ}$ ), and later crops (0.55 g.), which did not melt at  $340^{\circ}$ , were hydroxycaffeine contaminated with arsenic trioxide. The residual alcohol-soluble extract (0.45 g.), m. p.  $140-142^{\circ}$ , was identical with a prepared specimen of 8-ethoxycaffeine, the melting point of the mixture not being depressed.

**8-Hydroxycaffeine,** m. p.  $335^{\circ}$ , was readily prepared by heating 8-ethoxycaffeine with 16% hydrochloric acid for 10 minutes in the boiling-water bath. It was not obtainable directly from 8-chlorocaffeine by Fischer's process (*Ber.*, 1885, 28, 2486).

**8-Ethoxycaffeine** was prepared by heating 8-chlorocaffeine (1.5 g.) with potassium hydroxide (1 g.) and absolute alcohol (15 c.c.) under reflux on the water-bath for 6 hours. After removal of the solvent and extraction with water, 8-ethoxycaffeine (0.93 g.; yield, 62%), m. p.  $140-142^{\circ}$ , was collected; it crystallised in dense, colourless, waxy prisms.

**Phthalbromomethylimide.** When phthalbromomethylimide (2.4 g.) was heated with potassium arsenite (5 g.) in absolute alcohol (50 c.c.) under reflux for 7 hours, 0.9 g., m. p. ca.  $210^{\circ}$  (alone or mixed with phthalic acid), was collected, no other products being obtained. The experiment was repeated in acetone solution (50 c.c.) from

which 0.95 g. of product, m. p.  $230^{\circ}$ , was collected. This crystallised in colourless, rectangular prisms from glacial acetic acid, was very sparingly soluble in boiling water, and insoluble in ether (Gabriel, *Ber.*, 1887, **20**, 2225, gives m. p.  $232^{\circ}$  for ethylenediphtalimide) (Found: N, 8.8 by the Kjeldahl method.  $C_{13}H_{12}O_4N_2$  requires N, 8.7%).

*Action of Sodium Sulphite on Phthalbromomethylimide.*—The bromo-compound (9.1 g.) was boiled under reflux with sodium sulphite (75 c.c. of 20% aqueous solution; 2 mols.) until complete solution was effected ( $1\frac{1}{2}$  hours) and kept, when phthalimide (0.35 g., m. p.  $232^{\circ}$ ) was collected. The mother-liquor, on being acidified (Congo-paper), deposited phthalic acid (3.15 g., m. p.  $200^{\circ}$ ), whilst on concentration a further crop (0.85 g., m. p.  $200^{\circ}$ ; total yield 62%) was obtained. From the mother-liquors, by further concentration, phthalimidomethanesulphonic acid was obtained (1.2 g., m. p.  $270^{\circ}$  with decomp.; yield, 13.2%).

*Phthalimidomethanesulphonic acid* crystallises from water in long, fine, colourless, rectangular prisms, m. p. ca.  $295^{\circ}$  with decomposition according to the rate of heating; these contain  $2.5H_2O$ . After being dried at  $120^{\circ}$ , it does not melt even at  $320^{\circ}$ . It is very soluble in water, but almost insoluble in absolute alcohol (Found in air-dried substance: loss at  $120^{\circ}$ , 15.8.  $C_9H_7O_5NS \cdot 2.5H_2O$  requires  $H_2O$ , 15.7%. Found in substance dried at  $120^{\circ}$ : N, 5.9 by the Kjeldahl method.  $C_9H_7O_5NS$  requires N, 5.8%). The barium salt crystallises in long, fine needles which are sparingly soluble in water.

*Hydrolysis of the Sulphonic Acid.*—The sulphonic acid (0.5 g.) was heated with 20% hydrochloric acid (10 c.c.) for  $2\frac{1}{2}$  hours under reflux. On keeping, phthalic acid (0.3 g., m. p.  $214^{\circ}$ ; yield 91%) was obtained, whilst the mother-liquor on concentration gave less than 0.1 g. of ammonium chloride.

The author is greatly indebted to Dr. King for much helpful advice and criticism, and desires to thank Mr. W. Anslow for assistance in this investigation.

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## LXXIX.—*The Crystal Structure of Catechol.*

By WILLIAM AUGUSTUS CASPARI.

THE crystal morphology of catechol is known from the measurements of Beckenkamp (*Z. Kryst. Min.* 1900, **33**, 599), who assigned catechol to the monoclinic-prismatic class, axial ratios

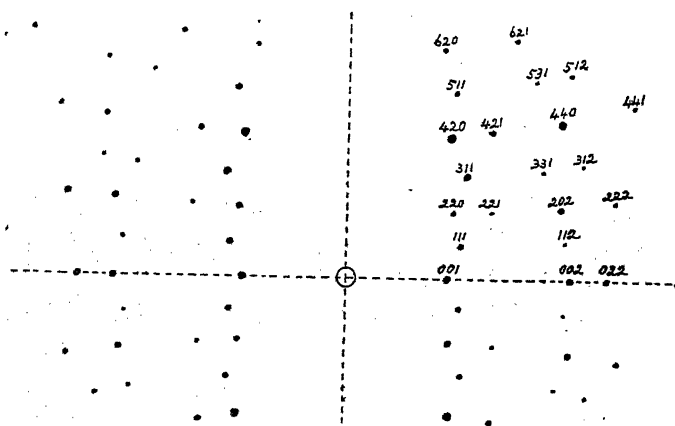
$U^*$

$1.6086 : 1 : 1.0229, \beta = 94^\circ 15'$ . In the present investigation, the rotating-crystal method has been used, and has led to definite data for the crystal cell and the space-group of catechol.

Perfectly developed crystals were obtained without difficulty by the slow evaporation of an aqueous solution. They were in most cases bounded by the three pinacoids; occasionally the prism  $\{110\}$  also appeared; swallow-tail twins about  $\{100\}$  were observed in a few instances.

X-Ray photographs were taken on glass plates through crystals set with the three crystallographic axes as rotation axes. The apparatus was of a simple character with a pinhole beam and requires no description; a Shearer tube with copper anticathode was used.

FIG. 1.

Catechol. Rotation axis  $a$ .

Figs. 1, 2, and 3 show the diagrams obtained by projecting the photographs on paper and marking the spots. As a rough guide to intensity, the size of the spots has been proportioned to the intensity of the photographic spots as far as possible. Spots due to  $K\beta$  radiation are omitted. The scale of the diagrams corresponds to a distance of 4.8 cm. between the plate and the crystal.

The dimensions of the unit cell follow directly from these photographs. Each spot represents the reflexion from a definite crystal plane, and the spots arrange themselves in layer lines upon which all planes have one index in common; these lines in the case of a flat plate take the form of hyperbolas. The spacing corresponding to the distance of the apex of the first hyperbola from the straight centre line is the length of the unit cell along the axis in question,

and those of further hyperbolas are consecutive multiples. Calculations are based on the formula

$$a(\text{or } b \text{ or } c) = n \times 1.54 / \cos \mu \text{ \AA.},$$

where  $n$  is the series number of the layer line, and  $1.54 \text{ \AA.}$  the wavelength of copper  $K\alpha$  radiation. The following cell dimensions were thus obtained:

$$\begin{array}{llll} \text{along } a \text{ axis, mean of 5 layer lines, } a = 17.46 \text{ \AA.} \\ \text{,, } b \text{ ,, ,, } 4 \text{ ,, ,, } b = 10.74 \text{ \AA.} \\ \text{,, } c \text{ ,, ,, } 2 \text{ ,, ,, } c = 5.48 \text{ \AA.} \end{array}$$

The ratios of these dimensions, *viz.*,  $1.62 : 1 : 0.51$ , agree with the goniometric axial ratios except that  $c$  has been stated at double its

FIG. 2.

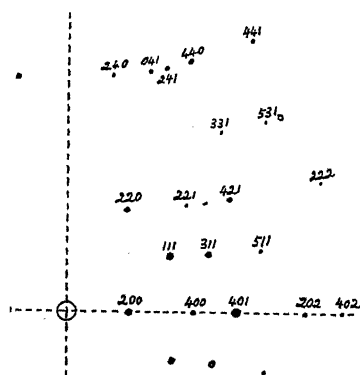
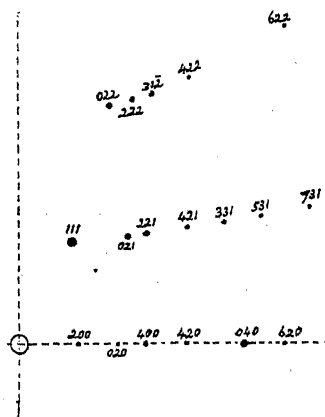
Catechol. Rotation axis  $b$ .

FIG. 3.

Catechol. Rotation axis  $c$ .

proper length by Beckenkamp. The axial ratios of catechol should be written  $1.6086 : 1 : 0.5114$ .

To find the number of molecules in the unit cell, we have as the weight of the cell, the density of catechol being  $1.375$ ,

$$17.46 \times 10.74 \times 5.48 \times \sin 94^\circ 15' \times 1.375 = 1403 \times 10^{-24} \text{ g.}$$

The weight of the molecule being  $110 \times 1.65 \times 10^{-24} \text{ g.}$ , the quotient is  $7.8$ . That is, there are eight molecules in the unit cell. Indices can now be assigned to the various photographic spots by calculating the spacing  $d$  of each and applying the stereometric formula proper to the monoclinic system, which in the present case takes the form

$$1/d^2 = 0.0033h^2 + 0.0087k^2 + 0.0331l^2 - 0.0016hl.$$

U\* 2

The indices of all the planes observed are tabulated below.

Rotation Axis a.			Rotation Axis b.			Rotation Axis c.		
Plane.	d obs.	d calc.	Plane.	d obs.	d calc.	Plane.	d obs.	d calc.
{001}	5.44	5.49	{200}	8.81	8.70	{200}	8.67	8.70
{002}	2.71	2.75	{400}	4.42	4.35	{020}	5.39	5.36
{022}	2.41	2.45	{401}	3.46	3.54	{400}	4.34	4.35
{111}	4.73	4.79	{202}	2.67	2.68	{420}	3.32	3.38
{112}	2.69	2.66	{402}	2.36	2.41	{040}	2.67	2.68
{220}	4.58	4.56	{111}	4.73	4.79	{620}	2.49	2.55
{221}	3.58	3.58	{311}	3.76	3.88	{111}	4.75	4.79
{202}	2.62	2.68	{511}	2.86	2.93	{021}	3.80	3.84
{222}	2.34	2.39	{220}	4.52	4.56	{221}	3.63	3.58
{311}	3.76	3.88	{221}	3.55	3.58	{421}	2.92	2.96
{331}	2.68	2.70	{421}	2.96	2.96	{331}	2.56	2.70
{312}	2.44	2.50	{222}	2.31	2.39	{531}	2.33	2.31
{420}	3.38	3.38	{331}	2.64	2.70	{731}	2.05	2.07
{421}	2.94	2.96	{531}	2.33	2.31	{022}	2.44	2.45
{440}	2.30	2.28	{240}	2.53	2.56	{222}	2.32	2.39
{441}	2.12	2.14	{041}	2.42	2.41	{312}	2.27	2.34
{511}	2.88	2.93	{241}	2.33	2.34	{422}	2.15	2.20
{531}	2.35	2.31	{440}	2.28	2.28	{622}	1.91	1.94
{512}	2.12	2.19	{441}	2.11	2.14			
{620}	2.55	2.55						
{621}	2.27	2.38						

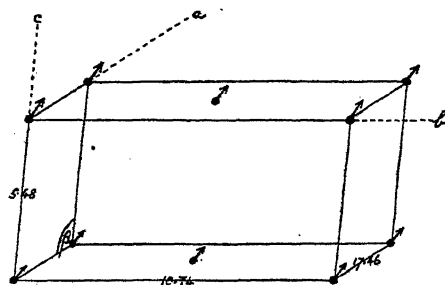


FIG. 4.

The table shows that in all cases the sum of the indices  $h$  and  $k$  is an even number, and that there are no other regularities connecting the various indices. From this it follows that if the cell be represented by four equal molecules at the corners of a parallelepiped, there must be molecules of the same orientation in the centres of the {001} faces (Fig. 4). Hence the space-lattice is  $\Gamma_m'$  and, further, the space-group is narrowed down to  $C_{2h}^3$ . For this space-group, eight asymmetric molecules is the full number permissible; the catechol molecule, therefore, is without any intrinsic symmetry in the crystalline state. Each primary molecule, as shown in Fig. 4, must have three other differently oriented molecules near it.

As regards the actual disposition of the molecules in the crystal, we have as arguments the above symmetry data, the crystal

habit, and the size and shape of the catechol molecule. The evidence at hand points to a simple parallelipipedic arrangement, such that all the molecules are as it were skewered along the  $b$  axis, with the plane of the benzene rings lying parallel to  $a$  and  $c$  and the hydroxyl groups pointing pairwise alternately backward and forward along the  $a$  axis. Detailed discussion may, however, be deferred pending the examination of 2:3-dihydroxynaphthalene and 2:3-dihydroxyanthracene, which is now in progress. The above arrangement is in harmony with the reticular densities of the crystal faces; these would work out as follows:

{100}	face,	1 molecule in	14.7 Å <sup>2</sup> .
{001}	„	„	23.5 „
{010}	„	„	48.0 „
{110}	„	„	57.0 „

In the majority of the crystals, {100} is decidedly the most developed and {010} the least developed face, whilst {110} occurs only sporadically; the order of the reticular densities is thus the same.

The author desires to express his indebtedness to Sir William Bragg, F.R.S., and to his fellow-workers at the Davy Faraday Laboratory for the helpful interest taken by them in this investigation; also to the authorities of the Royal Institution for apparatus and laboratory facilities.

DAVY FARADAY LABORATORY,  
ROYAL INSTITUTION.

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# LXXX.—*Unsymmetrically Substituted Dinitro- and Diamino-derivatives in the Stilbene and Tolane Series. Part I. The Elimination of Hydrogen Chloride from 3:4'-Dinitrostilbene Dichloride.*

By HAROLD AINSWORTH HARRISON and HAROLD WOOD.

FLÜRSCHHEIM was the first to point out the important principle that the alternate effects produced by substituents in aromatic nuclei can be rendered conspicuous by comparing the properties of isomeric  $m$ - and  $p$ -disubstituted derivatives. With groups in these two positions the possibility of ring closure is almost eliminated and anomalies caused by steric hindrance are largely curtailed, whilst the general polar effects are approximately equal. The present research was undertaken with the idea of testing the accuracy of

certain apparently unequivocal forecasts derived by application of the alternate polarity rule to the diphenylethane series. The theory of non-polar alternating affinity, on the contrary, does not appear to afford any trustworthy *a priori* guidance in the types of reaction selected for investigation.

The dichlorides and dibromides of  $\alpha\beta$ -unsaturated acids, when deprived of one molecule of halogen hydride, invariably lose the  $\beta$ -halogen atom. It seemed desirable, therefore, to ascertain whether similarly unidirectional influences could be discovered in the dihalides of unsymmetrically substituted stilbene derivatives. The effect of two nitro-groups in the 3- and 4'-positions is cumulative and a strong difference in the reactivity of the two halogen atoms should accrue. The removal of one molecule of halogen hydride should therefore result in the preferential formation of one or other of the two possible monochlorostilbenes. As a matter of fact,  $\alpha$ -chloro-4 : 3'-dinitrostilbene was the sole product of reaction, and this is in entire agreement with polarity principles.

3 : 4'-Dinitrostilbene had previously been prepared by Cullinane (J., 1923, 123, 2060) by the condensation of *p*-nitrophenylacetic acid and *m*-nitrobenzaldehyde in presence of piperidine at 100° for 1 hour. Exact repetition of his method by the present authors resulted, however, in the isolation of a totally different product. Cullinane's supposed dinitrostilbene consisted of yellow needles, m. p. 155° (yield not stated), which gave green solutions in various organic solvents. The dinitrostilbene obtained by us, having been washed many times with boiling alcohol and recrystallised from glacial acetic acid, melted at 217°, and was sparingly soluble in most solvents, forming only pale yellow solutions.

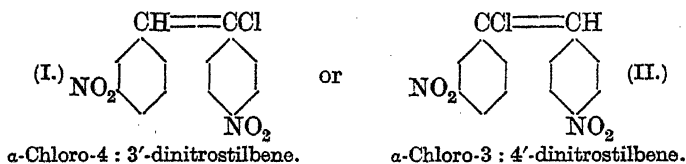
From the alcoholic washings three other products were isolated in small quantity: *p*-nitrotoluene, formed by the partial decomposition of *p*-nitrophenylacetic acid by piperidine, and the piperidine salts of the two stereoisomeric forms of 3 : 4'-dinitro- $\alpha$ -phenylcinnamic acid, resulting from loss of water without carbon dioxide. Both of these acids were subsequently synthesised. They could be decarboxylated to give the same dinitrostilbene by heating with piperidine. Their properties will be described in a future paper.

Preliminary investigation showed that 3 : 4'-dinitrostilbene dibromide\* on heating with pyridine lost both atoms of bromine; the stilbene was therefore converted into a mixture of dichlorides, from each of which (although with much greater facility in the case of the low-melting  $\beta$ -variety), by prolonged heating with pyridine, one

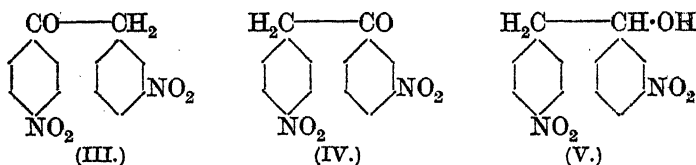
\* A detailed description of this dibromide will be given in a subsequent paper.



molecule of hydrogen chloride was eliminated, with the formation of only one monochlorodinitrostilbene, having one of the configurations I and II.



The chlorostilbene was eventually\* decomposed by warm concentrated sulphuric acid, with the formation of a coloured intermediate compound (not isolated). This on decomposition with water passed through the transitory enol form to produce 4-nitrophenyl 3-nitrobenzyl ketone (III).



That this ketone had the structure shown was proved by oxidising the intermediate aldol, 3:4'-dinitro- $\alpha\beta$ -diphenylethyl alcohol, isolated as a by-product from the stilbene condensation and therefore possessing the configuration (V), with chromic acid in acetic acid solution, when the isomeric 3-nitrophenyl 4-nitrobenzyl ketone (IV) was obtained.† Another proof of the constitution of (III), by its synthesis from 3:4'-dinitro- $\alpha$ -phenylcinnamamide, will be described shortly.

Each of these ketones (III and IV) was converted into the corresponding monochlorodinitrostilbene by treatment with phosphorus pentachloride, and although these two products melted at approximately the same temperature, a mixed melting point determination showed a depression of 20°, and further, each chlorodinitrostilbene, on treatment with sulphuric acid as before, was reconverted into the corresponding ketone.

Without doubt the monochlorodinitrostilbene formed by loss of the elements of hydrogen chloride from 3:4'-dinitrostilbene dichloride is I and not II.

\* Prolonged boiling with silver acetate in acetic acid, with potassium acetate, or with formic acid was ineffectual. An attempt to prepare the ozonide met with no greater success.

† Finzi had shown (*Monatsh.*, 1905, 26, 1128) that oxidation of a substituted deoxybenzoin to the benzil cannot be carried out with chromic acid in acetic acid.

## EXPERIMENTAL.

**3:4'-Dinitrostilbene.**—A mixture of *p*-nitrophenylacetic acid (76 g.) and *m*-nitrobenzaldehyde (63.5 g.) was heated with piperidine (13 g.) at 110° for 1 hour (carbon dioxide and water were expelled; the liquid then set to a semi-solid mass); thereafter the temperature was raised to 150°\* during 2 hours. The product was boiled with alcohol (200 c.c.) until the solid cake had disintegrated, and the dinitrostilbene was then filtered off, pulverised, and repeatedly washed with boiling alcohol (about 300 c.c.) until it was bright yellow. It crystallised from acetic acid, nitrobenzene or pyridine in yellow needles, m. p. 217° (Found: C, 62.35; H, 3.75.  $C_{14}H_{10}O_4N_2$  requires C, 62.2; H, 3.7%). It is slightly soluble in hot benzene, acetone, ethyl acetate, or chloroform, but very sparingly soluble in boiling alcohol. The yield was 30%. On standing, the mother-liquor and washings deposited a dark brown, viscous oil which could not be purified; treatment of this with cold strong sulphuric acid increased the total yield of dinitrostilbene to 55%.

**3:4'-Dinitro- $\alpha\beta$ -diphenylethyl Alcohol (V).**—After removal of this oil, addition of water precipitated a light yellow solid which, after crystallisation from acetic acid and then from alcohol, melted at 147–148° (Found: C, 58.1; H, 4.3.  $C_{14}H_{12}O_5N_2$  requires C, 58.3; H, 4.2%). This substance is soluble in alcohol, acetic acid, ethyl acetate, or acetone, and sparingly soluble in ether or benzene. Heating with piperidine or treatment with cold strong sulphuric acid produces the dinitrostilbene. Slow evaporation of the solution after removal of the aldol compound caused the separation of a little *p*-nitrotoluene, and on long standing the residual liquors deposited thin leaflets which crystallised from alcohol in straw-coloured needles, m. p. 168–169° (Found: C, 59.7; H, 5.2.  $C_{20}H_{21}O_6N_3$  requires C, 60.15; H, 5.3%). This compound is therefore the *piperidine* salt of one of the two stereoisomeric 3:4'-dinitro- $\alpha$ -phenylcinnamic acids, m. p. 221°.† If the temperature of condensation is allowed to rise to 160° after 1 hour, the yield of dinitrostilbene is even less than usual, much more *p*-nitrotoluene being formed. After removal of the normal reaction products (no pure aldol can be isolated) a crop of crystals separates, which after crystallisation from alcohol consists of bright yellow needles, m. p. 204–205° (decomp.) (Found: C, 59.85; H, 5.5.  $C_{20}H_{21}O_6N_3$  requires C, 60.15; H, 5.3%). This is the *piperidine* salt of the other stereoisomeric substituted cinnamic acid, m. p. 205.5°.†

\* Above this temperature much decomposition takes place.

† The free acids were obtained by treatment of the piperidine salts with warm sodium carbonate solution, and subsequent acidification; the melting points were not depressed by admixture with authentic samples.

*α- and β-Forms of 3:4'-Dinitrostilbene Dichloride.*—Finely divided 3:4'-dinitrostilbene (20 g.) was suspended in chloroform (750 c.c.),\* and dry chlorine passed in during 4 hours. After standing for 4 days, the excess of chlorine was removed from the filtered solution by shaking carefully with dilute sodium bisulphite, and then with sodium hydroxide. After having been washed and dried, the chloroform solution was evaporated to a small bulk until deposition of the dichloride commenced (concentration beyond this stage tends to blacken the product). When cold, the white crystals were filtered off, washed with a little chloroform, and dried (15 g.; 60% yield). They consisted of a mixture of the *α*- and *β*-forms, and melted at 188—196°. By two crystallisations from acetic acid the pure *α*-form could be obtained in thin plates, m. p. 207° (Found: Cl, 20.9.  $C_{14}H_{10}O_4N_2Cl_2$  requires Cl, 20.8%). The more soluble *β*-form, m. p. 132—138°, was never obtained quite pure (Found: Cl, 21.1%). Both forms are appreciably soluble in alcohol.

*α-Chloro-4:3'-dinitrostilbene (I).*—Preliminary investigation having shown that the *α*-modification of the dichloride is much more stable to pyridine than the *β*-, the crude mixture of dichlorides (75 g.) was heated (water-bath) with pyridine (160 g.) for 90 hours. On cooling, bright yellow, glistening needles of the monochloro-dinitrostilbene crystallised out, which after recrystallisation from acetic acid melted at 161° (Found: C, 54.9; H, 3.1; Cl, 11.5.  $C_{14}H_9O_4N_2Cl$  requires C, 55.2; H, 2.95; Cl, 11.6%). Precipitation of the mother-liquors with alcohol resulted in a further small quantity (total yield = 77%). No other product was isolated.† This compound crystallises well from pyridine, acetic or formic acid, benzene, chloroform, or acetone. It is but sparingly soluble in alcohol, ether, or carbon tetrachloride.

*4-Nitrophenyl 3-Nitrobenzyl Ketone (III).*—Finely powdered *α*-chloro-4:3'-dinitrostilbene (I) (5 g.) was gently warmed with strong sulphuric acid (20 c.c.) during 1 hour (above 60°, charring takes place). When the evolution of hydrogen chloride had ceased, the deep red solution was cooled and poured on to ice. The almost white precipitate was crystallised from alcohol, and then from acetic acid; clusters of white needles, m. p. 134°, were thus obtained

\* A smaller quantity of solvent is inadvisable, owing to the slow speed of absorption of chlorine by the stilbene.

† The liquors were concentrated almost to dryness on the water-bath and warmed with strong sulphuric acid. After the vigorous evolution of hydrogen chloride (chiefly from the pyridine hydrochloride) had ceased, the product was poured into water, and the lustrous deposit crystallised from alcohol (charcoal). It melted at 129° and did not depress the melting point of III. It had therefore been formed from the same chlorodinitrostilbene.

(Found: C, 58.5; H, 3.6.  $C_{14}H_{10}O_5N_2$  requires C, 58.7; H, 3.5%). This ketone is easily soluble in all the usual solvents except ether, light petroleum, or carbon tetrachloride. It gives a *semicarbazone* which crystallises from alcohol in pale yellow needles, m. p. 219°. Treatment of the ketone at its melting point with phosphorus pentachloride reconverted it into the monochlorodinitrostilbene.

**3-Nitrophenyl 4-Nitrobenzyl Ketone (IV).**—A solution of the aldol compound (V) (4.5 g.) in hot glacial acetic acid (45 c.c.) was cooled to 50° without allowing deposition of solid, treated with a 10% solution of chromic acid [prepared from crystalline sodium dichromate (7.5 g.), sulphuric acid (10 g.), and water (35 g.)] during 1 hour, and then, while still warm, with water (10 c.c.). The ketone which separated crystallised from 95% alcohol in pearly plates (yield 75%), m. p. 102° (Found: C, 58.65; H, 3.45.  $C_{14}H_{10}O_5N_2$  requires C, 58.7; H, 3.5%). The solubilities of this ketone approximate very closely to those of the isomeric ketone (III), m. p. 134°. It gives a *semicarbazone* which crystallises from alcohol in bright yellow rhombs, m. p. 230°.

**$\alpha$ -Chloro-3 : 4'-Dinitrostilbene (II).**—Treatment of the ketone (IV) at its melting point (brine-bath) with phosphorus pentachloride furnished the corresponding monochlorodinitrostilbene in fair yield; on crystallisation from acetic acid, it formed small clumps of light brown needles, m. p. 162° (Found: C, 55.0; H, 3.0; Cl, 11.8.  $C_{14}H_9O_4N_2Cl$  requires C, 55.2; H, 2.95; Cl, 11.6%). A mixture of the two isomeric monochlorostilbenes melted at 142–145°. The solubilities of this isomeride (m. p. 162°) are almost identical with those of the other (m. p. 161°). The degrees of stability, too, are comparable, since prolonged boiling with formic acid or with silver acetate in acetic acid does not remove the chlorine atom. Pyridine is also without action. Concentrated sulphuric acid at 60° converts it into the ketone (IV) from which it was derived, but so far as could be ascertained there was no difference in the rate of decomposition of the two monochlorodinitrostilbenes.

**Action of Concentrated Sulphuric Acid.**—The dinitrostilbene furnishes a bright red solution, from which the unchanged product is recovered on dilution with water: both monochlorodinitrostilbenes (I and II) give deep red solutions on warming and evolve hydrogen chloride vigorously; they char considerably at 80°: the dinitrostilbene dichloride yields a faintly pink solution, with very slight evolution of gas; it chars somewhat at about 80°: the dinitrostilbene dibromide gives a pink colour and evolves hydrogen bromide at 70–80°; there is no sign of charring, and the product after dilution with water and crystallisation from alcohol still contains bromine.

One of us (H. W.) desires to express his gratitude to the Department of Scientific and Industrial Research for a maintenance grant, and the other (H. A. H.) to the Chemical Society Research Fund for a grant which has defrayed the cost of materials. We are also indebted to Professor Lapworth for suggesting the line of research.

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## LXXXI.—*The Budde Effect in Bromine. Part I. The Photoactive Constituent of Wet Bromine.*

By BERNARD LEWIS and ERIC KEIGHTLEY RIDEAL.

THE experiments of Dixon and of Baker (*Rep. Brit. Assoc.*, 1894, p. 493; *J.*, 1884, 45, 611) on the influence of small traces of water on physical and chemical changes have led to the theory of internal equilibrium of Smits ("The Theory of Allotropy," Longmans and Co.) in which it is assumed that water acts as a catalyst in accelerating the attainment of equilibrium between various polymeric or allotropic forms of simple molecules in homogeneous systems which were originally in metastable states. To exert this catalytic activity it must be assumed that the water makes a temporary complex with the reactant, which complex must be capable of excitation or activation more readily than the reactant molecules themselves.

The earlier experiments of Budde (*Pogg. Ann.*, 1871, 144, 213; *Wied. Ann.*, 1879, 6, 477), Mellor (*J.*, 1902, 81, 1280), and Bevan (*Phil. Trans.*, 1903, 202, A, 71) as well as those of Pringsheim (*Wied. Ann.*, 1887, 32, 385), Richardson (*Rep. Brit. Assoc.*, 1888, p. 89), Shenstone (*J.*, 1897, 71, 471), and Cordier (*Monatsh.*, 1900, 21, 660) revealed the fact that dry chlorine differed from moist chlorine in that on exposure to radiation, especially in the blue and violet portion of the spectrum, moist chlorine underwent expansion, but dry chlorine, although absorbing the radiation, showed no such expansion. This "Budde" effect has likewise been noted by Budde (*loc. cit.*) and by Ludlam (*Proc. Roy. Soc. Edinburgh*, 1924, 44, 197) in the case of bromine.

The early experiments made it clear that the expansion in the moist halogen was due to the conversion of absorbed radiation into thermal energy of molecular agitation and it was assumed from this fact that, since the Budde effect is still obtainable in a region of the spectrum in which the quantum is small (in the case of bromine a Budde expansion is still noticeable at  $\lambda = 5800 \text{ \AA.}$ , whilst according to Franck [Photochemical meeting, Oxford, 1925], from a consideration of the distribution of the absorbed energy between

rotational, oscillatory, and electronic quantum states of the molecule, dissociation of the molecule cannot be effected with a wavelength greater than  $\lambda = 5000 \text{ \AA.}$ ), the thermal effects are not produced by a primary activation of a bromine molecule followed by a splitting into atoms with their subsequent recombination. It has also been shown by Sir J. J. Thomson (*Proc. Camb. Phil. Soc.*, 1901, 11, 90) that the formation of charged ions according to the reaction  $\text{Br}_2 \rightleftharpoons \text{Br}^+ + \text{Br}^-$  does not occur, a view which can likewise be demonstrated to be improbable from a comparison of the magnitudes of the energies required for dissociation into atoms and ions respectively. How the moisture caused the conversion of radiant into kinetic energy was not elucidated. We may note, however, that Bevan (*loc. cit.*) postulated the existence of complexes such as  $(\text{Cl}_2)_x(\text{H}_2\text{O})_y(\text{H}_2)_z$  in the water-sensitised hydrogen-chlorine mixture, and on analogy with this conception it might be argued that a hydrate  $(\text{Br}_2)_x(\text{H}_2\text{O})_y$  was the photoactive constituent responsible for the Budde effect. Alternatively it might be suggested that in the metastable, freshly distilled, dry halogen a photosensitive polymeride of bromine is absent, but is present when the inner equilibrium is attained with the aid of the catalytic water. With the exception of the work of Coehn and Jung (*Z. physikal. Chem.*, 1924, 110, 705) on the hydrogen-chlorine reaction, no quantitative work on the influence of water on such reactions has been accomplished and it appeared of interest to examine the Budde effect in bromine in more detail.

It may be stated at the outset that the experimental data support the hypothesis that the Budde effect is due to a photosensitive bromine hydrate of composition  $\text{Br}_2 \cdot \text{H}_2\text{O}$  and that the water does not function as a catalyst in the formation of a photosensitive polymeride of bromine. Having established this point, it was necessary to investigate the properties of this hydrate in more detail such as its heat of formation, the value of the equilibrium constant of the reaction  $\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O} \cdot \text{Br}_2$  and the distribution of the hydrate, *i.e.*, the partition of the hydrate between the surface and bulk phases in the reaction vessel.

Finally, it was decided to investigate how far the absorption spectrum of the hydrate differed from that of bromine vapour, to evaluate its absorption coefficient, and to suggest a hypothesis as to the mechanism of operation of the Budde effect.

The importance of these points would appear not to be confined to the Budde effect alone, for if hydrates do exist in the gas or liquid phases of non-polar, or feebly polar substances, it is to be anticipated that the walls of the containing vessel which adsorb water readily will likewise adsorb the hydrate. Thus the partition

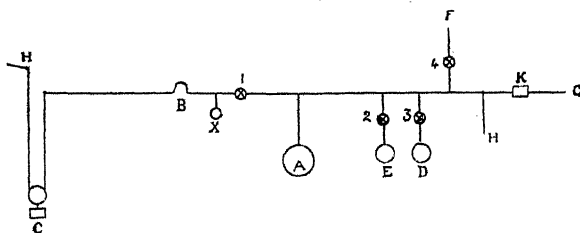
of the hydrate between the bulk and surface phases will obey an equation of the type found to hold in the isothermal adsorption of vapours and will prove an important factor in the relative rates at which reactions, which are *ex hypothesi* due to this hydrate, occur in the two phases.

Again, whilst dry bromine does absorb light within a large portion of the spectral region which causes the Budde effect in wet bromine, no thermal effects are to be noted. It follows that the apparent absorption is fictitious, for the light must be re-emitted as fluorescent light or scattered from the molecules. The hydrate molecules, on the other hand, absorb the light which is subsequently converted into thermal energy. The data from absorption spectra clearly do not distinguish between these two phenomena. The influence of water in cutting down the fluorescence of dry hydrogen and oxygen exposed to illumination of a quartz mercury vapour light recently noted by Baker\* (J., 1925, **127**, 1990) and the fluorescence of dry active hydrogen yielding the line  $\lambda = 3064 \text{ \AA.}$ , a water vapour line (Bonhoeffer, *Z. physikal. Chem.*, 1925, **116**, 39), would appear to be a phenomenon similar to that occurring in bromine.

#### EXPERIMENTAL.

Two forms of apparatus were employed for determination of the effect of alteration in the partial pressures of the bromine and

FIG. 1.



water on the magnitude of the Budde effect. For low partial pressures of water, the following method was devised. The reaction vessel, *A*, of 20 c.c. capacity, consisted of a bulb with plane-parallel sides, 2.35 cm. apart, connected on one side by capillary glass tubing to the phosphoric oxide tube, *X*, and the glass gauge, *B*. On the other side capillary connexions were made to the bromine and water reservoirs *D* and *E*, the drying train, *F*, the McLeod gauge, *H*, and mercury vapour pump line, *G*.

During evacuation of the reaction vessel the gauges and reactant

\* Communicated at a meeting of the Society.

reservoirs were temporarily disconnected by capillary glass inner seals 1, 2, 3, 4, which were provided with iron rods enclosed in glass permitting of fracture of the seals with the aid of an electromagnet. Between the diffusion pumps, *G*, and the apparatus a liquid air-trap was placed to prevent back-diffusion of mercury vapour. The gauge, *B*, consisted of a well-annealed (5 months), collapsed elliptical glass bulb forming a Bourdon indicator, attached to a 30 cm. glass pointer, to the end of which one arm of a quartz bifilar suspension for a mirror, *C*, was attached. The mirror was steadied by means of a mica vane dipping in water, the surface tension of which was lowered by the addition of a drop of oleic acid, thus permitting unhindered movement of the mirror. A spot of light from the mirror on a scale one metre away was followed. The sensitivity of the gauge could be varied by alteration, with the aid of a micrometer screw, of the position of the left arm, *H*, of the bifilar suspension; pressure changes of 1/120 mm. of mercury could be registered when it was in most sensitive adjustment. The gauge was calibrated with the aid of a mercury manometer and eye-piece, frequent calibration showing but little change in the characteristics.

The apparatus employed for the higher vapour pressures of water was similar to that described above, but in place of internal seals, stopcocks, lubricated by two rims of chlorinated odourless wax, were employed. In place of the water reservoir, a bulb containing sodium sulphate decahydrate was employed as source of water vapour, which was connected to the reaction vessel and pump through a small dosing apparatus of 0.3 c.c. capacity permitting of admission of small quantities of water vapour to the dry bromine. The source of light was a 1000 c.p. point light, parallel rays being obtained with a collimator, the reaction vessel being mounted in a plane-sided trough through which water was circulated from a thermostat. Between the collimator and the trough was placed a smaller trough in which the requisite colour filters could be placed.

*Materials.*—The bromine was prepared by distillation of the purest obtainable bromine, twice over zinc oxide and once over freshly prepared phosphoric oxide in a closed system which had originally been baked out. The bromine was stored over phosphoric oxide in a sealed vessel and was not used for the dry experiments until 9 months later. The data of Ramsay and Young (1886, 49, 453) were employed for the vapour pressure at various temperatures.

The sodium sulphate decahydrate was prepared by triple crystallisation and partial desiccation. The dissociation vapour pressure



at 0° employed was 2.77 mm., from the value given by Baxter and Lansing in the Landolt-Bornstein tables.

The water employed was pure conductivity water, and the vapour pressures were calculated with the aid of the equation of Nernst (*Verh. deut. physikal. Ges.*, 1907, **11**, 313):  $\log_{10} P_{\text{mm.}} = -\frac{2611}{T} + 1.75 \log T - 0.00210T + 6.5343$ , substantiated experimentally to 100° K. by S. Weber (*Communication Lab. Leyden*, 1915, **14**, 150A).

Three different vapour pressures were employed at temperatures corresponding to the freezing points of toluene, ethyl acetate and chloroform. The values are in the following table:

Substance.	Temperature.	V. p. above the ice in mm. Hg.
Melting toluene .....	-93°	$3.9 \times 10^{-5}$
„ ethyl acetate .....	-83	$2.3 \times 10^{-4}$
„ chloroform .....	-63	$5.3 \times 10^{-3}$

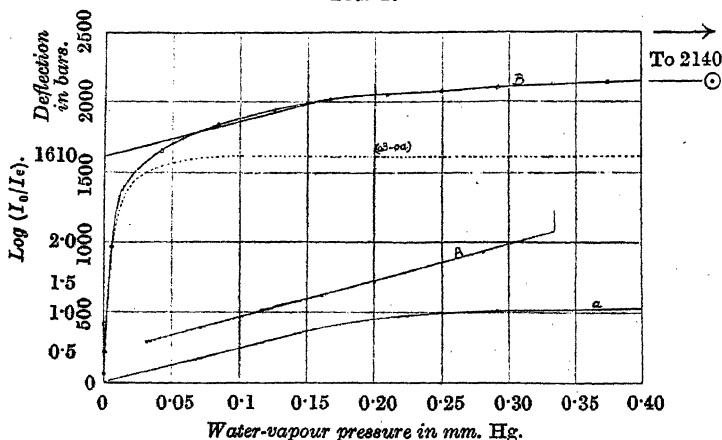
*Method of Operation.*—The method of operation employed was as follows. The reaction vessel was placed in an electric furnace and the capillaries and connexions up to the seals were wound with nichrome wire and thoroughly lagged with asbestos. One or two small parts were heated frequently with a Bunsen flame. A vacuum (less than  $10^{-6}$  mm. Hg) was maintained in the system at 400° for 5 days. The seal connecting the system to the ice maintained in liquid air was first broken with the connexion still open to the pumps. The high vacuum was rapidly reached again, the pumps were disconnected, the liquid air was replaced by melting toluene, and the water vapour allowed to pass into the reaction bulb. When equilibrium was attained (over an hour), the capillary tube leading to the water-vapour container was sealed under the blow-pipe, and the reservoir removed. Dry bromine at the required partial pressure (the bromine reservoir had been previously evacuated and maintained at a desired temperature) was admitted, and the bromine reservoir removed in a similar manner. Finally, dry air was admitted to atmospheric pressure, and the connexion sealed. The phosphoric oxide tube, X, was sealed and the connexion to the gauge established by breaking the capillary seal (1). Finally, the tube containing the iron rod at seal (1) was sealed and removed.

The reaction vessel was brought to a uniform temperature by the circulating water, and the deflection on the gauge observed for various distances of the lamp and with various colour filters (Wratten light filters). Finally, the gauge setting was calibrated. Four separate experiments were carried out in this manner, one with dry bromine-air mixture, in which no Budde effect was noted under the most intense illumination, and three with water vapour at the partial pressures given above.

For determination of the Budde effect at higher water-vapour pressures, taps instead of internal seals were employed and evacuation was effected with a Toepler pump instead of the diffusion pumps. On admission of dry bromine and air to the reaction vessel a small Budde effect was always noticeable under strong illumination, indicating that traces of water vapour (0.001 mm.) could not be eliminated entirely by this procedure.

To admit definite quantities of water to the evacuated system, the sodium sulphate reservoir at 0° was opened to the 0.3 c.c. capillary doser, thus filling it with water vapour at a partial pressure of 2.77 mm. Bromine was admitted to the reaction vessel, and then dry air passed through the doser into the 20 c.c. bulb,

FIG. 2.



thus sweeping the water vapour into the reaction system. Any number of doses could be admitted in this manner.

Neither with air nor with dry bromine on illumination was the slightest change in pressure observed, but in the presence of moisture a rapid rise in pressure, approaching an equilibrium value within 20 to 30 seconds, was always obtained. On cutting off the illumination, the light spot of the gauge indicator returned to its initial position.

An investigation of the magnitude of the Budde effect with various light filters showed (the Wratten filters 15, 16, 21, 25 as well as various combinations were permeable to photochemically active light) that light of wave-length longer than  $\lambda = 5800 \text{ \AA}$ . produced no detectable effect; light within a region  $5600 \text{ \AA}$ . to  $5500 \text{ \AA}$ . was particularly effective. Accordingly, a filter combination transmitting red light and light from  $5400 \text{ \AA}$ . to  $5700 \text{ \AA}$ .

with a maximum permeability near 5500 Å. was employed for all quantitative experiments.

An investigation revealed that the energy distribution in the various wave-lengths between 5000 Å. and 6000 Å. of the point light as measured with a thermopile and galvanometer was uniform, thus a mean of the effective extremes of the light filter could be assumed.

*Results.*—In the curve (Fig. 2) is given the relationship between the Budde effect in bars (dynes per sq. cm.) as a function of the partial pressure of the water vapour at a constant bromine pressure of 158 mm. and a temperature of 40°. Some of the values obtained, from which the curve was plotted on a very large scale so as to permit of accurate analysis, are in the following table :

Partial press. of Br, 158 mm. Temp. of bath, 40°. Distance of lamp, 15 cm.

Press. of H <sub>2</sub> O in mm. Hg.	Deflection in bars.	Press. of H <sub>2</sub> O in mm. Hg.	Deflection in bars.
0	0	$8.3 \times 10^{-2}$	1830
$3.9 \times 10^{-5}$	66	$1.245 \times 10^{-1}$	1950
$2.3 \times 10^{-4}$	226	$1.66 \times 10^{-1}$	2020
$5.0 \times 10^{-3}$	958.8	$3.32 \times 10^{-1}$	2140
$4.15 \times 10^{-2}$	1640	$5.395 \times 10^{-1}$	2140

It will be noted that the curve may be divided into three portions; for low partial pressures of water up to 0.005 mm. the Budde effect rises rapidly; this is followed by an almost linear portion of the curve (0.03 mm. to 0.16 mm.) in which the Budde effect increases proportionally to the increase in the water-vapour pressure; finally, at high water concentrations, the Budde effect increases less rapidly, attaining a maximum of *ca.* 2140 bars at a partial pressure of 0.3320 mm., which is not affected even when the water-vapour pressure is increased to 0.5810 mm. It was suspected that this apparent maximum as well as that shown in Fig. 3 was due to complete absorption of the active radiation. Proof of the correctness of this view was obtained in the following ways. The Budde effect for these high water concentrations was found to be dependent on the distance of the source of illumination from the bulb as shown by the following data, *a* being the distance (cm.) of the lamp from the reaction vessel, and *b* the deflection in scale-divisions :

<i>a</i> .....	72	62	52	42	32	22	15.5	11
<i>b</i> .....	5	7	10	16	25.5	44—45	82	160

It might indeed be argued that the flattening of the curve is caused by increased heat radiation outward, as the Budde effect increases. In the following manner this view was found to be incorrect, within the magnitudes of the Budde effect, and our first view more directly confirmed. A very fine platinum filament,

terminating in thick platinum wires, was sealed in the reaction vessel, which was filled with bromine and water vapour to the desired partial pressures. Several partial pressures of bromine were employed. An electric current was passed through the spiral filament and from a knowledge of the current passing and the potential difference across the spiral the heat evolution in calories per second to give various expansions measured on the gauge could readily be determined. Fig. 4 shows the curve, average values of deflections for different bromine concentrations (these varied only a little) being plotted as ordinates against calories per second developed by the spiral as calculated from  $H = 0.24RI^2$ . It will be observed that the curve bends only slightly within the limits employed. If, now, one takes two deflections on curve A (Fig. 3) and plots as abscissa the heat corresponding, as obtained from Fig. 4, and then from this interval one obtains the scale plotting in place of bromine pressure as abscissa, the calories per sec. (Curve C), one observes that the two curves coincide along the rectilinear portion. It is clear that if the falling off of the Budde effect were due to increased heat radiation, the two curves should coincide throughout. But the Budde effect falls off much more rapidly, supporting the view that the maximum is due to complete absorption of the actinic rays.

The following furnishes additional proof for the total extinction of the actinic rays at the maximum. When the surface is practically saturated, the course of the curve is governed by the absorption of light in accordance with Beer's law.

$$I_e = I_0 e^{-k(dc+K)}$$

where  $K$  is the constant concentration of hydrate on the surface (see later, p. 593).

Hence  $\log(I_e/I_0) = -k(dc + K)$  or  $\log(I_0/I_e) = k'c + K'$ .

$C$ , the concentration of the hydrate, is proportional to the water concentration in the bulk phase. Curve A (Fig. 2) shows that from 0.03 mm., where the surface concentration is practically up to saturation, this proportionality holds true until complete absorption of the light.

Over a certain pressure range the Budde effect increases proportionally to the increase in the partial pressure of the water vapour.

In Fig. 3 are plotted the Budde effects as functions of the partial pressures of bromine at the constant water-vapour pressures of 77 mm. (A) and 0.20 mm. (B), respectively, and at 40°, the distances of the lamp from the bulb being 21 and 32 cm., respectively. Above partial pressures of bromine of ca. 20 and 40 mm., respec-

tively, the curves follow the same course as those noted for the constant bromine-variable water-vapour pressure curves, *viz.*, the Budde effect is proportional to both the partial pressure of the bromine and of the water vapour. Such a relationship is most readily interpreted on the assumption that the photoactive constituent responsible for the Budde effect is a bromine hydrate of composition  $\text{Br}_2 \cdot \text{H}_2\text{O}$  in mass equilibrium with the reactants according to the equation

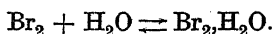
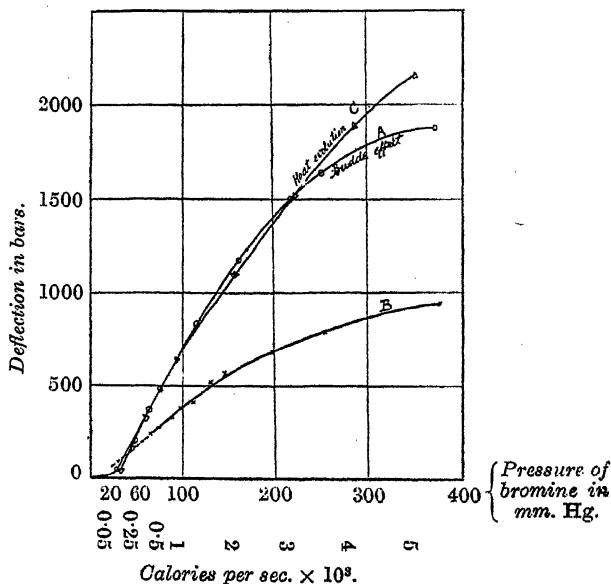


FIG. 3.

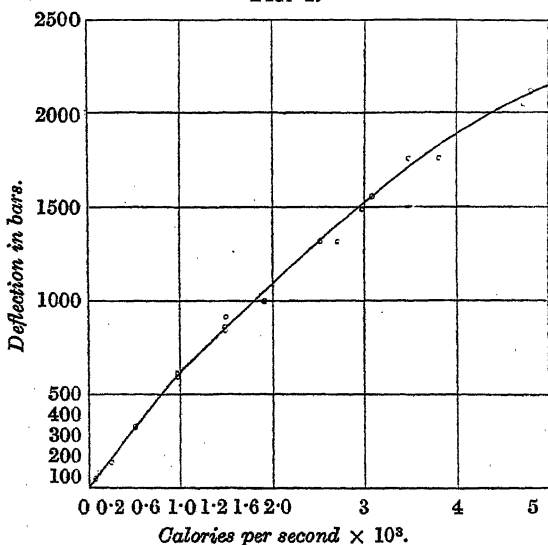


In the light of this hypothesis the convex form of the curve for low water-vapour pressure (Fig. 2) and the concave form of the constant water-vapour pressure curves at low bromine pressures (Fig. 3) are significant.

It is clear that when the partial pressures of water are low (below 0.005 mm.) the Budde effect rises more rapidly than we should be led to expect from application of the law of mass action to the bulk phase. If bromine hydrate were strongly adsorbed by the walls of the glass vessel, the surface concentration increasing with the partial pressure until a saturation maximum was attained at about 0.10 mm., the reason for this increase of the Budde effect at low partial pressures of water vapour and the convex form of the curve when the walls are dry would be clear. Again, if in the

presence of high pressures of water and low partial pressures of bromine the walls of the vessel are covered with water, the Budde effect will consequently be proportional to the bromine hydrate in the gas phase at the commencement, but will rise more rapidly as the pressure of the hydrate increases and displacement of the adsorbed water by the latter commences, thus explaining the initial concave form of the curves for low bromine and high water-vapour pressures. With low partial pressures of water (Fig. 3, curve B) it will be seen that the displacement of water from the surface by the hydrate commences at a lower partial pressure. After this initial curvature the curve rises in a linear manner proportional

FIG. 4.



to the quantity of bromine hydrate present both in the surface and the gas phases.

Such a view, which is advanced from a knowledge of the hygroscopic nature of glass and the convex and concave forms of the bromine-water-vapour pressure curves at low partial pressures, is greatly strengthened by careful analysis of the convex curve. The Budde effect is, according to this view, due to absorption of light by bromine hydrate which is present both in the bulk phase and on the surface of the glass. The curve at low partial pressures of water is thus the effect of both the bulk and the surface concentrations. The bulk concentration increases in a linear manner with increase in water-vapour pressure until the light absorption becomes great, and this portion contributes a Budde effect given

by the line *oa* (Fig. 2). The surface concentration at various partial pressures contributes a Budde effect given by the curve *oB—oa*. If this be the case, it should be capable of expression in the form of an adsorption isotherm. Since it is probable that the water vapour and hydrate layer is but one molecule thick, the partial pressures being far lower than those employed by McHaffie and Lenher (J., 1925, 127, 1559), where multimolecular layers were formed, the Langmuir isotherm should be applicable:

$$x = ap/(1 + bp),$$

where  $x$  = the surface concentration of the hydrate or is proportional to the Budde effect in the surface,  $p$  = the partial pressure of the hydrate in the gas phase or is proportional to the concentration of water, and  $a$  and  $b$  are constants.

The prolongation of the rectilinear portion of the curve, where the surface is hydrate-saturated, intersects the ordinate at 1610 bars. This, then, is the limit to the Budde effect produced by the surface phase.

Hence when  $p$  is large,  $x = a/b = 1610$ ,  
 for  $p = 0.0005$ ,  $300 = 0.0005a/(1 + 0.0005b)$ .  
 From which we obtain  $b = 458$ ,  $a = 7.38 \times 10^5$ .

The following table shows the calculated and the observed values (in bars) of the Budde effect in the surface phase for increasing water-vapour pressures.

Partial press. of H <sub>2</sub> O (mm.).	$x$ calc.	$x$ obs.	Partial press. of H <sub>2</sub> O (mm.).	$x$ calc.	$x$ obs.
$3.9 \times 10^{-5}$	28.4	66	0.01	1320	1200
$2.3 \times 10^{-4}$	154	226	0.03	1500	1500
$5.0 \times 10^{-4}$	300	300	0.08	1573	1590
$5.0 \times 10^{-3}$	1100	950			

Taking into consideration the difficulties of evaluating the actual values of the Budde effect for the initial portion of the curve, which is extremely steep, the agreement between the observed and the calculated values does not exceed the experimental error.

The bromine hydrate which is the photoactive constituent responsible for the Budde effect is thus present in the reacting system both on the walls of the containing vessel and in the homogeneous gas phase, the distribution between surface and bulk phases obeying the usual adsorption isotherm equation.

In order to confirm the view that even at low partial pressures of water vapour there was adsorbed on the walls of the containing vessel a relatively large quantity of hydrate even when the bulk concentration was low, the following experiment was devised.

A small horizontal cell 4 cm. long and 1.25 cm. in diameter with

plane glass ends was constructed. Inside the cell a round coverslip was placed in a vertical plane so that the light passed through the ends of the cell and through the coverslip; a gentle shaking of the cell permitted the coverslip to fall down so that the narrow circular beam of light now passed only through the ends of the cell and the gas phase. Behind the cell a small Moll thermopile was placed so as to obtain a measure of the radiation absorbed by the cell. In addition, the cell was connected to the glass gauge and bromine reservoir in the usual manner.

The following data were obtained on illumination with light passing the colour filters employed in the previous investigation.

<i>Expt. 1.</i>	Cell.	Gas in cell.	Thermopile galvo. deflection.	Budde effect.
Coverslip up.	Air.		22.27	nil
" "		Bromine at 104 mm.	20.23	7—8 av. 7.5
Coverslip down.	" "	" "	21.15	4
" "	Air.	" "	22.27	nil

It will be noted that with air, the position of the coverslip did not affect the amount of light falling on the thermopile, indicating absence of scattering, reflection or absorption of the light due to the glass. When the coverslip was up, the light passed through four glass-gas interfaces and when down through but two such interfaces, the former producing a larger Budde effect and a larger light absorption. If the amount of hydrate in the homogeneous gas phase be denoted by  $x$ , producing a Budde effect,  $kx$ , and a light absorption,  $lx$ , and that on each glass-gas interface be denoted by  $y$ , producing effects  $ky$  and  $ly$ , respectively, we obtain the following relationships:

(a) From the Budde effect.

$$4y + x = 7.5k \quad \text{and} \quad 2y + x = 4k,$$

whence  $2y = 3.5k$  and  $x = 0.5k$ ,

or 12.5% of the Budde effect is produced by hydrate in the gas phase and 87.5% produced by hydrate on the two flat ends of the cylinder.

(b) From the absorption of light.

$$4y + x = 2.04l \quad \text{and} \quad 2y + x = 1.12l,$$

whence  $2y = 0.92l$  and  $x = 0.20l$ ,

or 17.8% of the Budde effect is produced by hydrate in the gas phase and 82.2% produced by hydrate on the two flat ends of the cylinder.

A repetition of this experiment with a bromine pressure of 140 mm. with the same water-vapour pressure gave the following values:



	Coverslip up.	Coverslip down.
Absorption .....	3.06	1.75
Budde effect .....	12	7

whence we obtain the following percentages for the distribution of the hydrate :

	% In bulk phase.	% On surface phase.
From Budde effect .....	28	72
From absorption of light .....	25.3	74.7

As the concentration of hydrate is increased by elevation of the bromine pressure, the bulk concentration of hydrate increases more rapidly than the surface concentration, which, as shown in the previous experiments, finally approaches a surface saturation maximum. From Fig. 2 the percentage of the maximum Budde effect caused by the surface phase is 75, and that of the volume 25 under the experimental conditions.

In Fig. 3 the initial concave portion of the curve was attributed to the effect of the surface adsorption of water vapour which when present in large quantities could displace bromine hydrate when present in but small quantities, *i.e.*, at low partial pressures of bromine.

To confirm this view, both the light absorption and the Budde effect for the bromine in the small cell were determined for low and high partial pressures of water. If excess of water displaces the adsorbed bromine hydrate from the glass surfaces, we should anticipate that, in spite of the increase of the bromine hydrate in the bulk phase due to the addition of water, the removal of the bromine hydrate by displacement from the walls will cause a diminution in the total Budde effect. The following data were obtained :

Cell containing	Deflection for thermopile.	Budde effect.	Absorption.
Air .....	25.49	0	—
Bromine at 144 mm. ....	22.49	11	3.00
Bromine at 144 mm. and H <sub>2</sub> O vapour at 18° .....	23.12	9	2.37

The diminution in the Budde effect on a very large increase in the partial pressure of water is clearly brought out.

#### *Summary.*

The Budde effect in bromine is shown to be proportional to both the partial pressure of bromine and of water vapour and is probably due to a photoactive bromine hydrate of composition Br<sub>2</sub>.H<sub>2</sub>O. This hydrate is strongly adsorbed by glass surfaces and the relationship between the concentration in the bulk and the surface phases can be expressed in the form of an adsorption iso-

therm. The hydrate may be displaced from glass surfaces by water. The Budde effect was not observed on illumination of moist bromine with light of wave-length longer than  $\lambda = 5800 \text{ \AA}$ .

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## LXXXII.—*The Budde Effect in Bromine. Part II.* *The Kinetics of the Reaction and the Light Absorption of Wet and of Dry Bromine.*

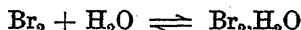
By BERNARD LEWIS and ERIC KEIGHTLEY RIDEAL.

In Part I evidence was presented for the view that the photo-active constituent responsible for the Budde effect in moist bromine is a bromine hydrate of composition  $\text{Br}_2 \cdot \text{H}_2\text{O}$  which is present both in the homogeneous gas phase and on the walls of the containing vessel. The adsorption isotherm equation was shown to be applicable to the partition of the hydrate between the two phases.

It was considered of interest to examine the properties of this bromine hydrate in more detail.

### *The Equilibrium Constant and Heat of Formation.*

From a determination of the Budde effect at various temperatures the alteration of the equilibrium



can be determined. The determinations were carried out with the apparatus described in the previous communication. A low partial pressure of water was employed so that the Budde effect was due almost entirely to the adsorbed bromine hydrate. The following values were obtained,  $t$  being the temperature of the bath, and  $K/K_p$  the deflection in scale divisions:

$t$ .....	99°	81°	63°	41°	22°
$K/K_p$ .....	86	95	106	122	140

The deflection decreases, or the equilibrium constant,  $K_p$ , where

$$K_p = [\text{Br}_2][\text{H}_2\text{O}]/[\text{Br}_2 \cdot \text{H}_2\text{O}],$$

increases, with elevation of the temperature.

Since an intense light was employed and the bromine hydrate concentration was low, the deflection is proportional to the concentration of the hydrate on the surface and may be employed in the van 't Hoff isochore to calculate the heat of formation.

Inserting the above values in the equation

$$2.3 \log_{10} \frac{K_1}{K_2} = \frac{Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

we obtain the following values (in calories) for  $Q$ :  $Q_{81^\circ} = 1440$ ,  $Q_{63^\circ} = 1425$ ,  $Q_{41^\circ} = 1340$ ,  $Q_{22^\circ} = 1336$ .

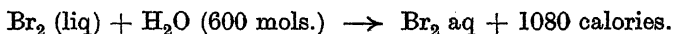
Since  $Q_t = Q_0 + \beta T^2$ , where  $2\beta$  = the difference in specific heat of reactants and products, we obtain

$$\beta = 0.0028 \text{ and } Q_0 = 1090 \text{ cal.}$$

Thus the heat change in the formation of the hydrate in the surface phase can be expressed as follows:



The magnitude of  $Q_0$  is in agreement with expectations regarding the heat of formation of such an unstable compound; it is practically identical with the heat change on solution of bromine in water:



From a knowledge of the heat of reaction it is possible, with the aid of the approximation equation of the Nernst heat theorem, to calculate the value of the equilibrium constant.

Inserting the values  $Q_0 = 1090$  (if there is a difference in the heat of formation in the surface phase and the bulk phase it cannot be very large, for the heat of formation is already so small. We may therefore without serious error assume 1090 cal. as the heat of formation in the bulk phase),  $T = 313^\circ \text{ K}$ ,  $\Sigma \nu = 1$ , and  $\Sigma \nu C = 3$  in the equation

$$\log_{10} K_p = \frac{-Q_0}{4.571T} + 1.75 \Sigma \nu \log T + \Sigma \nu C,$$

we obtain  $\log_{10} K_p = 6.61$  or  $K_p = 4.10 \times 10^6$  in atmospheres =  $3.10 \times 10^9$  in mm.

From this value we find that with a partial pressure of bromine of 200 mm. and of water vapour of 10 mm. the partial pressure of the hydrate will be  $0.65 \times 10^{-6}$  mm., equivalent to a concentration of  $3.86 \times 10^{-11}$  g.-mol. per litre in the bulk phase.

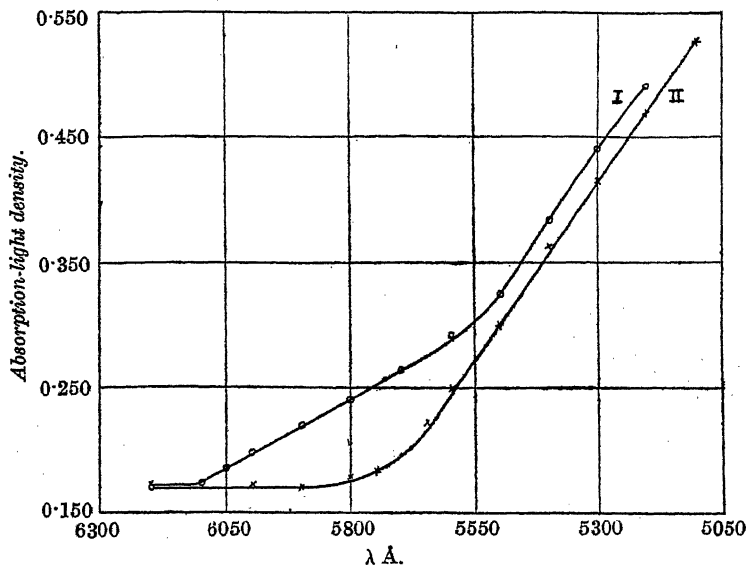
The increase of pressure on illumination has been taken as a measure of the equilibrium constant at various temperatures. Such a procedure is justified, since the Budde effect has already been shown to be proportional to the concentration of the hydrate and the large value of  $K_p$  for the equilibrium constant indicates that the equilibrium concentration of the hydrate is always so small that even large alterations in its concentration due to alteration in the temperature cannot affect the concentration of bromine or water, which may be regarded as constant.

*The Absorption Spectrum.*

If this small quantity of bromine hydrate is the photoactive constituent, it must possess properties different from those of dry bromine. An examination of the absorption spectra of wet and of dry bromine revealed interesting differences.

In Fig. 1 are plotted the absorption curves for wet and for dry bromine determined with the aid of a Nutting spectrophotometer (zero = 0.173), the dry bromine being retained in a clear quartz polarimeter tube which, previously to the admission of bromine,

FIG. 1.



I. Wet bromine. II. Dry bromine.

stored over phosphoric oxide for 9 to 10 months, had been thoroughly ignited whilst a high vacuum was maintained in the system.

The curves indicate that whilst ordinary bromine in wet vessels commences to show a definite absorption at  $\lambda = 6100$  Å., the dry bromine shows no marked absorption before  $\lambda = 5700$  Å. If light absorption is taken as a criterion of molecular excitation, the complex bromine-water requires an energy of excitation 3200 calories per g.-mol. less than that of dry bromine (2.05 volts compared with 2.20 volts) and it might be suggested that the catalytic effect of water vapour in many reactions may in part be due to the lower critical energy increment required for excitation of the complex hydrate.

Whilst the absorption of radiation by the hydrate results in the degradation of the radiant energy, dry bromine absorbs radiation of light of  $\lambda = 5700 \text{ \AA}$ . This light, however, does not reappear as thermal energy, for dry bromine shows no Budde effect. It must be concluded that such light which does not pass through the tube and is not degraded to heat must be either reflected or absorbed and re-emitted by the dry bromine molecules in the direction of the sides of the tube, *i.e.*, must be emitted as resonance radiation or fluorescence. In the presence of water vapour more light is absorbed and fluorescence would be reduced. The possible extinction of such fluorescence in dry bromine by water vapour would appear to have its counterpart in the extinction of fluorescent mercury by gases such as hydrogen and water vapour noted by Stuart (*Z. Physik*, 1925, 32, 262) and the extinction of fluorescence by water vapour in hydrogen and oxygen mixtures noted by Baker. It would further suggest the emission and absorption of light from molecule to molecule in a dry gas until absorption by a hydrate molecule occurred as a mechanism for chain reactions. Several experiments were devised to detect the difference between the nature of the light emitted from the sides of narrow tubes containing wet and dry bromine respectively, down the axes of which narrow pencils of yellow light were passed. Whilst no quantitative data could be obtained, the light emitted from the dry bromine appeared somewhat yellower, *i.e.*, richer in the rays absorbed by bromine, than the reddish light from the wet tube.

*The Stark-Einstein Law of Photoequivalence.*

An attempt was made to establish the validity of the Stark-Einstein law of photochemical equivalence in the case of the Budde effect. The measurements of the absorption of energy by the reaction vessel containing bromine were made with a black-body radiation meter. The meter consisted of a flat black receiving bulb with compensator and aniline gauge and was calibrated by the method of internal electric heating with the aid of a small platinum spiral in the interior; the whole system being carefully lagged and preserved from any slight air currents which might affect either the steadiness or accuracy of reading. Due corrections were made for the resistance of the circuit and leading-in wires. The following calibration values were obtained :

Room temperature 20.2°.		Ergs per sec. per 10 div. $\times 10^{-4}$ .
Reading in scale div.	Cal./sec.	
3.5	$5.36 \times 10^{-4}$	6.42
4.7	$7.73 \times 10^{-4}$	6.83
6.8	$1.29 \times 10^{-3}$	7.93
10.7	$2.55 \times 10^{-3}$	10

x 2

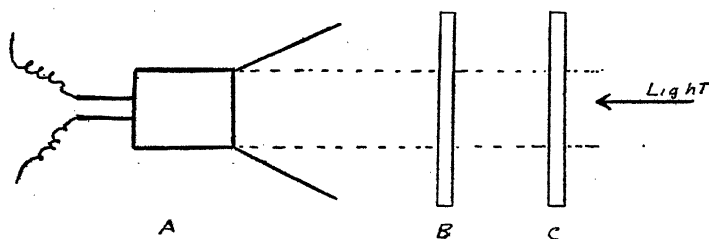
In a typical experiment with light between 5300—5700 Å. it was found that the bromine absorbed energy, as measured by the radiation meter, of  $1.53 \times 10^4$  ergs per second, yielding a Budde effect of 184.8 bars.

As has already been indicated, part of the light apparently absorbed by the bromine, *i.e.*, not transmitted to the radiation meter, is emitted from the sides of the tube in the form of fluorescence. It was necessary to find out how much of the energy of  $1.53 \times 10^4$  ergs per second was emitted as fluorescence, *i.e.*, apparently absorbed by dry bromine, and how much contributed to the Budde effect by absorption by the bromine hydrate. The following arrangement (Fig. 2) was accordingly devised to evaluate this fraction:

A. Moll thermopile.

B. A reaction vessel similar to C containing moist bromine at the same partial pressure, or air.

FIG. 2.



C. Reaction vessel containing either dry bromine in contact with phosphoric oxide, or air.

The two reaction vessels were of similar size and shape, both with plane and parallel sides immersed in a trough through which water from a thermostat was circulated. The point light lamp, water trough, collimator, and screens were used as heretofore. After the lamp had been so adjusted that a constant deflection was obtained on the Moll thermopile with the bulbs containing dry air, dry bromine was first admitted to bulb C at a partial pressure of 120 mm. The deflection on the thermopile was noted and moist bromine (saturated at 17°) admitted to B until the partial pressures of the bromine in the two bulbs were identical. The deflection was again noted and the bromine in the bulb C was replaced by dry air; the final determination of the radiation transmitted to the thermopile was then made. These operations were repeated, reversing the procedure in each case, and the following average readings were obtained:

B containing air	bromine } 24.80	B containing dry air	} 25.43
C containing dry		C containing dry air	
	B containing moist bromine		} 23.97.
	C containing dry air		

These results indicate that the apparent absorption by dry bromine is represented by 0.63 division on the Moll thermopile, that by wet bromine by 1.46 divisions; or about 43.2% of the light apparently absorbed by the moist bromine is emitted again in the form of radiation, as it does not contribute to the thermal energy to which the Budde effect is due.

The areas under the absorption curves between wave-lengths 5400 Å. and 6100 Å. will give the percentage absorptions due to wet and to dry bromine (wet bromine absorbs up to 6100 Å.; the filter transmitted the red rays):

Area under dry curve = 3130. Area under wet curve = 6530.

% absorbed by dry  $\text{Br}_2$  = 48. % absorbed by wet  $\text{Br}_2$  = 52.

All the light absorbed by the unhydrated bromine in the wet bromine is not emitted as fluorescence from the sides of the vessel. A part of it is reabsorbed by the hydrated molecules and degraded into heat energy. What proportion is reabsorbed we have no means of determining from our data. It must be borne in mind that as far as the absorption spectra curves are concerned it makes no difference how much of the emitted light is reabsorbed, since only a small portion of this light, even if not reabsorbed, would find its way through the spectrophotometer.

Accordingly, of the  $1.63 \times 10^4$  ergs per second apparently absorbed, or not transmitted by the wet bromine, in the previous experiment, 56.8% is actually absorbed and 43.2% emitted as radiation, or  $0.926 \times 10^4$  ergs per second are absorbed. The mean wave-length of light employed was 5550 Å., for the energy distribution curve of the radiation passing through the filter was flat within the region 5300 Å.—5800 Å. or the mean quantum was  $3.53 \times 10^{-12}$  erg; the number of quanta actually absorbed by the bromine hydrate per second is accordingly  $0.926 \times 10^4 / 3.53 \times 10^{-12}$  or  $2.62 \times 10^{15}$  quanta per second.

The Budde effect was 184.8 bars, corresponding to a heat evolution, as determined from the curve given in Part I, of  $1.26 \times 10^4$  ergs per second. If this heat is evolved by the conversion of quanta of magnitude  $3.53 \times 10^{-12}$  erg into kinetic energy in the decomposition or deactivation of the excited bromine hydrate molecules, we obtain as the number of molecules undergoing such a process of deactivation or decomposition per second  $1.26 \times 10^4 / 3.53 \times 10^{-12}$  or  $3.57 \times 10^{15}$ .

In the following table are the results of three different experi-

ments performed in the above manner. Figures in the third column are obtained by multiplying the calibration value in the previous table by 1.11 to allow for diffusive reflection of lampblack.

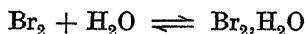
Exp. Temp.	Mano- meter diff.	Total ergs per sec. not trans- mitted $\times 10^{-4}$ .	Quanta per sec. absorbed by the hydrate $\times 10^{-15}$ .	Budde effect in bars.	Ergs per sec. equiv- alent $\times 10^{-4}$ .	Mols. per sec. decom- posing $\times 10^{-15}$ .	Mols. per quanta.
2 20.8°	2.28	1.63	2.62	184.8	1.26	3.57	1.36
3 20.9	2.43	1.73	2.78	186	1.30	3.68	1.32
4 20.2	1.73	1.24	2.00	149	1.01	2.82	1.41

These calculations were made under extreme conditions allowing for no absorption by the hydrate molecules of the re-emitted radiation from dry bromine. Taking this into account would bring the figures in the last column close to unity.

However, it will be noted from the data in the last column that the agreement between the number of quanta absorbed per second by the hydrate and the number of such molecules decomposing per second with the liberation of the energy of activation in the kinetic form is sufficiently close to show the validity of the Stark-Einstein law of photoequivalence in the case of the Budde reaction.

#### *The Absorption Coefficient of the Hydrate.*

On the hypothesis that the photoactive constituent is a bromine hydrate it is possible from a consideration of its concentration and the magnitude of the Budde effect, which is a measure of the light actually absorbed by the hydrate, to effect a determination of the absorption coefficient. The actual bulk concentration of hydrate for definite partial pressures of bromine and water can be determined only on the assumption that the concentration equilibrium of the reaction



is not sensibly affected whether the water vapour and the hydrate are in the surface or bulk phases, an assumption which is only valid if the activity coefficients of the reactants do not change sensibly during adsorption, or that the change in the activity coefficient of the water on adsorption is the same as the change effected in this function of the bromine hydrate. Since the heat of formation of bromine hydrate is small, some measure of support is given to the latter hypothesis. We will therefore employ the value for  $K_p$  determined above as  $3.10 \times 10^9$  when expressed in mm. of mercury.

From the curves given in Fig. 2 (Part I of this investigation), in which the increase in Budde effect with increasing water-vapour pressure at a constant bromine pressure is plotted, it is seen that at a pressure of 0.0415 mm. of water and a pressure of 158 mm.



of bromine, a Budde effect of 115 bars was caused by the bromine hydrate in the gas phase, out of a total of 2140 bars (maximum deflection under the intensity of illumination employed).

Thus 5.4% of the light was absorbed by the bromine hydrate present in the gas phase, which was 2.35 cm. deep, or 94.6% would have been transmitted if no surface phase existed. The partial pressure of the hydrate in the gas phase can with the proviso indicated above be determined with the aid of the equilibrium constant or

$$[\text{Br}_2][\text{H}_2\text{O}]/[\text{Hydrate}] = 3.10 \times 10^9 = 158 \times 0.0415/[\text{Hydrate}],$$

whence the partial pressure of the hydrate is  $2.1 \times 10^{-9}$  mm. From Beer's law,  $I_t = I_0 e^{-kcd}$ , where  $I_0$  is the entering light,  $I_t$  the transmitted light,  $c$  the concentration,  $d$  the thickness, and  $k$  the absorption coefficient of the hydrate, we obtain :

$$\log_e (I_t/I_0) = -kcd,$$

$$\text{or} \quad 2.3 \log_{10} 0.946 = -kcd = -k(2.1 \times 10^{-9}) \times 2.35,$$

$$\text{whence} \quad k = 10.7 \times 10^6.$$

In a similar manner, for a point where  $P_{\text{H}_2\text{O}} = 0.083$  mm. we find a Budde effect, in the gas phase, of 230 bars or 10.75% light absorption, whence  $I_t/I_0 = 0.8925$  and  $k = 11.4 \times 10^6$ . For the low partial pressure of  $P_{\text{H}_2\text{O}} = 0.02$  mm. we find a Budde effect in the gas phase of 55 bars, equivalent to 2.57% light absorption or 97.43% light transmitted, whence  $k = 9.6 \times 10^6$ . The mean value of the absorption coefficient is thus  $10.5 \times 10^6$ .

It is interesting to compare this value with that obtained by Wood (*Physikal. Z.*, 1912, **13**, 353) for the absorption of the light ( $\lambda = 2537 \text{ \AA.}$ ) by mercury vapour. He found that the intensity of this light was reduced by one-half by passage through a layer of mercury vapour 5 mm. thick and at a partial pressure of  $10^{-4}$  mm. Inserting these values in the equation, we obtain

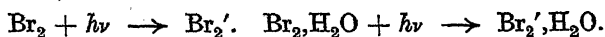
$$2.3 \log_{10} 0.50 = -k \times 10^{-4} \times 0.5, \text{ whence } k = 0.14 \times 10^6.$$

Thus the absorption coefficient of bromine hydrate in the spectral region which produces excitation is comparable in value with that of mercury vapour for its resonance line. On the hypothesis of Ornstein that the range of influence of a quantum of light is proportional to the square of the wave-length, the absorption coefficient of bromine hydrate for light of  $\lambda = 5550 \text{ \AA.}$  should be some four times that of mercury vapour.

#### *Mechanism of the Budde Effect.*

The first elementary process in a photochemical action is, as Stern and Volmer (*Z. Wiss. Photographie*, 1920, **19**, 275) were the

first to show, not the primary reaction but the excitation of the molecule by absorption of radiation. On the hypothesis that there exist in moist bromine both bromine and bromine hydrate molecules, the primary processes of light absorption are the conversion of these into active molecules:



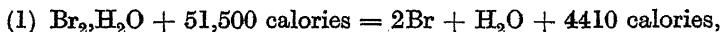
We have seen that in the case of dry bromine no Budde expansion occurs, although light absorption undoubtedly takes place. The excited bromine molecules must thus lose their energy of excitation in the form of radiation. Whether the radiation emitted from an excited bromine molecule in the interior of the gas passes through the gas to the outer walls or undergoes a series of absorptions and emissions from numerous molecules in the operation of transfer of a quantum from the interior to the surface, or, again, whether the energy of the excited molecule is handed on by collision within the life of the excited molecule, *viz.*,  $10^{-7}$  second, thus forming a chain, cannot be established with certainty. As in the case of the resonance line of mercury vapour, if the light is emitted from the bromine molecules as light of the same wave-length as the absorbed light, the course of the fluorescent light is interrupted in its path to the surface by its absorption by hydrate molecules, thus materially reducing the strength of the fluorescent light.

We have seen that only when a bromine molecule is moist, *viz.*, a bromine hydrate, do we obtain a Budde effect or conversion of the light energy into thermal energy. The frequency,  $\nu$ , of any line may be considered as the sum  $\nu = \nu^e + \nu^n + \nu^m$ , where  $e$  is the electronic,  $n$  the oscillatory, and  $m$  the rotational quantum number (Mulliken, *Physical Review*, 1925). In absorbing a quantum, not only may the quantum level of the electron be changed, but also the oscillatory and rotational quantum energy levels. In the case of iodine at low pressures (Oldenberg, *Z. Physik*, 1923, 18, 1), the molecule, without dissociating, can absorb and re-emit as a resonance spectrum an amount of energy five times the work of dissociation when it is illuminated by light of wave-length  $\lambda = 1849 \text{ \AA}$ . The explanation advanced is that the excitation energy is primarily employed in raising the electron system to a higher quantum state, whilst the oscillation and rotation energies are only altered by the coupling of their periods with those of the electron system. But we may have, in the case of the halogens, marked changes in the oscillation energy where the absorption of light alters the potential energy of the nuclei, thus altering the strength of chemical binding of the molecule. In the excited electronic state, the energy required for dissociation is less than in the normal state, and if the alteration

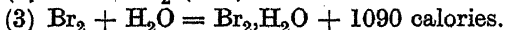
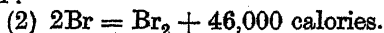
in the oscillation quanta is sufficient to cause the potential energy of the nuclei to become greater than the dissociation energy for the excited state the molecule will fly apart. There is indeed a correlation between a large change in oscillation quantum number and a considerable alteration of the strength of binding on excitation. As a measure of the strength of binding we can utilise, for qualitative estimates, the direction of the shading of the bands, which is an indication of change in the moment of inertia of the molecule. The band spectra of iodine investigated by Mecke (*Ann. Physik*, 1924, **71**, 104) show a convergence limit of the oscillation quantum states at 5000 Å. Wave-lengths, therefore, of 5000 Å. or less will dissociate iodine under certain conditions. The convergence limit for bromine has been placed by Franck (see Part I, *loc. cit.*) at about the same wave-length from the position of the long wave-length limits of the continuous spectra which are known.

The light used in this investigation being of considerably greater wave-length, dry bromine would not be expected to dissociate. That dissociation does not occur is proved further by the work of Ludlam (see Part I, *loc. cit.*), who found no Budde effect with dry bromine illuminated with ultra-violet light containing energy many times that necessary for dissociation.

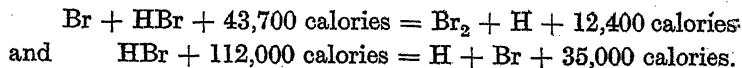
It would appear that in the case of bromine hydrate the lowering of the critical energy increment for dissociation into atoms is very great. Dissociation may occur thus :



where 51,500 calories is the energy of the radiation of wave-length employed in these experiments, some 4410 calories greater than the threshold value, as is confirmed by the commencement of absorption at 6100 Å. The recombination of the bromine and water to re-establish equilibrium gives rise also to the evolution of the heats of combination :



The same type of mechanism is given by the calculations of Christiansen (*Dansk Vid. Math. Phys. Medd.*, 1919, **1**, 14) for the reactions



Thus 47,090 calories appears to be close to the critical energy that must be absorbed by bromine hydrate before any Budde effect can be expected. The absorption of light of greater frequencies, for a given constant quanta absorption, merely increases

the heat effect on the right-hand side of the equation (1) and thus the Budde effect.

*Summary.*

The heat of formation of bromine hydrate is 1090 calories, comparable with the heat of solution of liquid bromine in water, whilst the equilibrium constant for the dissociation of bromine hydrate at 313° K is of the order of  $3 \cdot 10 \times 10^9$ . The absorption curves of wet and of dry bromine have been compared; marked absorption commences at  $\lambda = 6100 \text{ \AA.}$  for the wet and at  $\lambda = 5700 \text{ \AA.}$  for the dry gas; this corresponds to a lowering of the critical energy increment of excitation of 3200 calories. When corrected for the absorption and probable fluorescence of dry bromine, it is found that the Stark-Einstein law of photoequivalence is obeyed, a maximum of 1.41 molecules per quantum being obtained. The absorption coefficient of bromine hydrate for the spectral region employed is  $10 \cdot 5 \times 10^6$ , comparable with that obtained by Wood,  $0 \cdot 14 \times 10^6$ , for mercury vapour for the line  $\lambda = 2537 \text{ \AA.}$  A mechanism of excitation and decomposition of bromine hydrate molecules is advanced in explanation of the Budde effect.

Our thanks are due to Messrs. Brunner Mond for a grant which enabled us to purchase the apparatus necessary for this research.

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LXXXIII.—*Studies of Valency. Part V. Absorption Spectra of Halogen and Sulphonic Derivatives of Camphor: Origin of the Ketonic Absorption Band.*

By THOMAS MARTIN LOWRY and GLYN OWEN.

1. *Scope of the Work.*

THE preceding paper on absorption spectra (Lowry and French, "Studies of Valency," Part IV, J., 1924, 125, 1921) dealt with the selective absorption of camphor and of some of its conjugated derivatives. Its principal feature was an experimental proof of the existence in camphorquinone and in methylenecamphor of two different types of conjugation, corresponding perhaps with the presence of "crossed" and of "concordant" polarities in these two compounds. In the present paper, these experiments have been extended to a series of halogen derivatives of camphor, for which data were required in connexion with measurements of rotatory

dispersion (J., 1925, 127, 1260). The absorption spectra of some of these compounds had been plotted previously by one of us (Lowry and Desch, J., 1909, 95, 807), but only by the old qualitative method of recording the last line transmitted through a given thickness of solution in sufficient intensity to leave a record on the photographic plate. These observations were therefore not sufficiently exact for a quantitative comparison, the ultimate result of which was to reveal the existence of a small discrepancy between the characteristic frequencies deduced from measurements of rotatory dispersion and those obtained by recording directly the maximum value of the molecular extinction coefficient.

The original purpose of the experiments demanded only a knowledge of the characteristic frequency of the band of selective absorption; but the data in Table I have an interest of their own, which exceeds that of the approximate coincidence of the frequencies deduced by the two methods referred to above. Thus, not only have we been able to draw more exact conclusions as to the effect of halogens on the familiar absorption band of the ketone, but the "general absorption" of the compounds, which can now be investigated just as accurately as their "selective absorption," has been found to present striking characteristics, especially with regard to the mutual influence of negative radicals (compare Part VII, following paper). In this way the observations have provided important clues as to the origin and significance of selective and general absorption in carbon compounds generally.

## 2. *Experimental Methods.*

Camphor- $\beta$ -sulphonic acid, and four camphorsulphonates containing a halogen atom, were examined in aqueous solutions. The fifteen other halogen derivatives were all examined in *cyclohexane*. This solvent was selected in order to conform as closely as possible to the conditions under which the rotatory dispersions of many of these compounds had been measured in benzene (J., 1925, 127, 807). The choice of *cyclohexane* as an alternative to benzene (which was not sufficiently transparent for measurements of absorption) was justified by the fact that some of its physical properties approximate very closely to those of benzene (Gifford and Lowry, *Proc. Roy. Soc.*, 1923, A, 104, 430) and in particular that the wave-length of maximum absorption for a solution of camphor in *cyclohexane* had been found to be the same as for a thin film of camphor in benzene (Lowry and French, J., 1924, 125, 1924). Apart from these considerations, however, *cyclohexane* has proved to be a good solvent for measurements of absorption, since, although unpurified specimens are not very transparent, and may even exhibit an absorption band,

the material can be purified readily by repeated shaking with 100% sulphuric acid on a mechanical shaker. When washed with water and distilled, it was then found to be transparent to about 2200 Å.U., which is approximately the limit of transmission of the calcite of the ultra-violet spectrophotometer.

The fifteen halogen derivatives of camphor and the five sulphonates had all been purified by crystallisation, and in most cases the samples had already been used for measurements of rotatory dispersion.

The methods of measurement were the same as in Part IV of this series of papers, absolute values being recorded for the "molecular extinction coefficients" at different wave-lengths up to the limit of transparency of the solution. As a rule, about 60 measurements were made with each compound, at concentrations ranging from  $M/4$  to  $M/400$ ; but the experimental points were too numerous to be inserted in the figures, except in one case (Fig. 7), where the range of wave-lengths and intensities made it possible to plot the data on a larger scale.

### 3. *Summary of Experimental Results.*

The present series of observations has proved that, whilst the presence of a halogen influences both the selective and the general absorption of the compounds, and affects these two properties in a somewhat similar manner, the two influences are sufficiently independent to produce large variations in the "persistence" of the band,\* *i.e.*, in the relative separation of the accessible band of "selective" absorption and the inaccessible band of "general absorption" as measured by the depth of the trough between them. The experimental results, which are summarised in Table I, may therefore be discussed most conveniently under these two headings.

(a) *Selective Absorption.*—The principal results are as follows:

(i) The general proposition, that the position of the ketonic band is largely independent of the nature of the ketone, is confirmed, since the wave-length of maximum absorption ranges only from 2880 Å.U. in camphor to 3230 in  $\alpha'$ -dibromocamphor. The intensities also cover only a small range from  $\log \epsilon = 1.4$  to 2.0. This is in marked contrast with the conjugated systems examined in Part IV, where the value of  $\log \epsilon$  rose from 1.4 in camphor to 4.3 in benzylidene-camphor.

(ii) A halogen in the  $\alpha$ -position produces a marked "intensification" of the selective absorption, since it increases both the wave-length and the maximum extinction coefficient of the ultra-

\* It is therefore unlikely that the general absorption of these compounds is a mere harmonic of the selective absorption.

TABLE I.

*Selective and General Absorption of Halogen and Sulphonic Derivatives of Camphor.*

No. of curve.	Substance.	Selective absorption.				Persist- ence log $\epsilon$ (max.), -log $\epsilon$ (min.).	General absorption	
		Maximum. log $\epsilon$ (max.).	Minimum. log $\epsilon$ (min.).			$\lambda$ for log $\epsilon$ = 1.5.	log $\epsilon$ for $\lambda$ = 2500.	
		$\lambda$ max.	$\lambda$ min.					
(a) <i>In cyclohexane.</i>								
I.	Camphor.	2880	1.45	<2327	<-0.26	<1.72	None at 2400 Å.U.	
II.	$\alpha$ -Chlorocamphor.	3050	1.72	2510	0.67	1.05	<2300*	0.68
	$\alpha'$ -Chlorocamphor.	3060	1.75	2550	0.94	0.81	<2300*	0.97
III.	$\alpha$ -Bromocamphor.	3100	1.95	2700	1.20	0.75	2590	1.83
	$\alpha'$ -Bromocamphor.	3120	1.95	2720	1.26	0.69	2530	1.96
IV.	$\beta$ -Bromocamphor.	2930	1.89	2750	0.98	0.41	2370	1.12
V.	$\alpha\alpha'$ -Dichlorocamphor.	3100	1.82	2570	0.22	1.60	2400	0.40
VI.	$\alpha\alpha'$ -Bromochloro- camphor.	3150	1.84	2840	1.57	0.27	†	2.45
VII.	$\alpha\alpha'$ -Dibromocamphor.	3230	1.88	2970	1.74	0.14	†	2.86
VIII.	$\alpha$ -Chloro- $\beta$ -bromo- camphor.	3060	1.67	2600	0.73	0.94	2400	1.3
IX.	$\alpha$ -Bromo- $\beta$ -chloro- camphor.	3080	1.87	2690	1.40	0.47	2630	1.9
X.	$\alpha\beta$ -Dibromocamphor.	3080	2.03	2700	1.46	0.57	2680	2.5
XI.	$\alpha\pi$ -Dichlorocamphor.	3080	1.68	2590	0.40	1.68	2370	0.5
XII.	$\alpha$ -Bromo- $\pi$ -chloro- camphor.	3150	2.01	2610	0.59	1.42	2490	1.45
XIII.	$\alpha\pi$ -Dibromocamphor.	3120	2.05	2670	1.09	0.96	2590	1.83
	$\alpha'\pi$ -Dibromocamphor.	3090	2.02	2680	0.80	1.22	2560	1.85
(b) <i>In water.</i>								
XIV.	Camphor- $\beta$ -sulphonic acid.	2850	1.54	2390	0.50	1.04	2300	‡
XV.	Potassium $\alpha$ -chloro- camphor- $\beta$ -sulphon- ate.	3000	1.59	2510	0.50	1.09	2300	0.51
XVI.	Potassium $\alpha$ -bromo- camphor- $\beta$ -sulphon- ate.	3030	1.93	2640	1.39	0.54	2600	1.90
XVII.	Ammonium $\alpha$ -chloro- camphor- $\pi$ -sulphon- ate.	3030	1.85	2660	1.00	0.85	2500	1.50
XVIII.	Ammonium $\alpha$ -bromo- camphor- $\pi$ -sulphon- ate.	3020	2.09	2630	1.50	0.59	2630	1.90

\* In these compounds, the general absorption is very weak and log  $\epsilon$  does not rise to 1.5 within the limits of our experiments; the value of  $\lambda$  corresponding to log  $\epsilon$  = 1.5 could therefore only be deduced by extrapolation.

† In these two compounds, where the general absorption is very strong, the molecular extinction coefficient falls to a minimum (at log  $\epsilon$  = 1.6 and 1.75 respectively), and then begins to rise again towards the crest of the band of selective absorption, but it never falls as low as log  $\epsilon$  = 1.5.

‡ In this compound, where the general absorption is very weak, the band of selective absorption extends to a minimum at about 2400 Å.U.; the general absorption does not begin, therefore, until the wave-length is already less than 2500 Å.U.

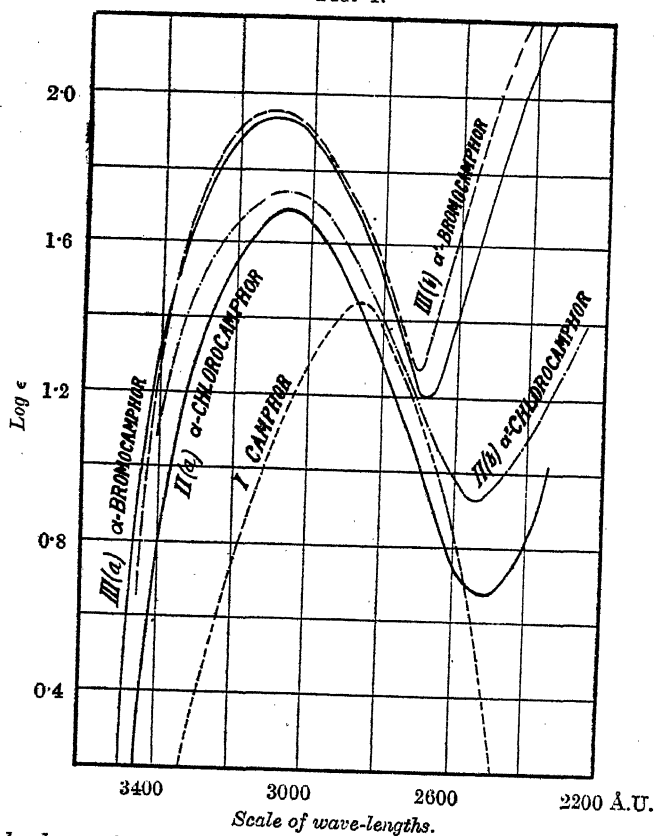
violet band (Fig. 1). The influence of an atom of bromine in the  $\beta$ -position is, however, almost negligible, since an insignificant increase of wave-length is balanced by an equally unimportant diminution in the maximum extinction coefficient (Fig. 7). The conclusion reached in an earlier paper (J., 1909, 95, 817) that, whilst a halogen atom in a  $\alpha$ -position produces an "intensification" of the band, an atom of bromine in the  $\beta$ - or  $\pi$ -position, has a "repressive action," is therefore no longer valid when applied to the selective absorption alone instead of to the "persistence" of the band.

(iii) The data for the  $\alpha\beta$ - and  $\alpha\pi$ -derivatives (Figs. 3 and 4)

confirm the conclusion that an atom of bromine in the  $\beta$ - or  $\pi$ -position produces only negligible changes in the wave-length and penetration of the band, and certainly has no "repressive" action.

(iv) The most striking intensification of the selective absorption is seen in the  $\alpha\alpha'$ -dihalogen derivatives (Fig. 2). In this group of

FIG. 1.



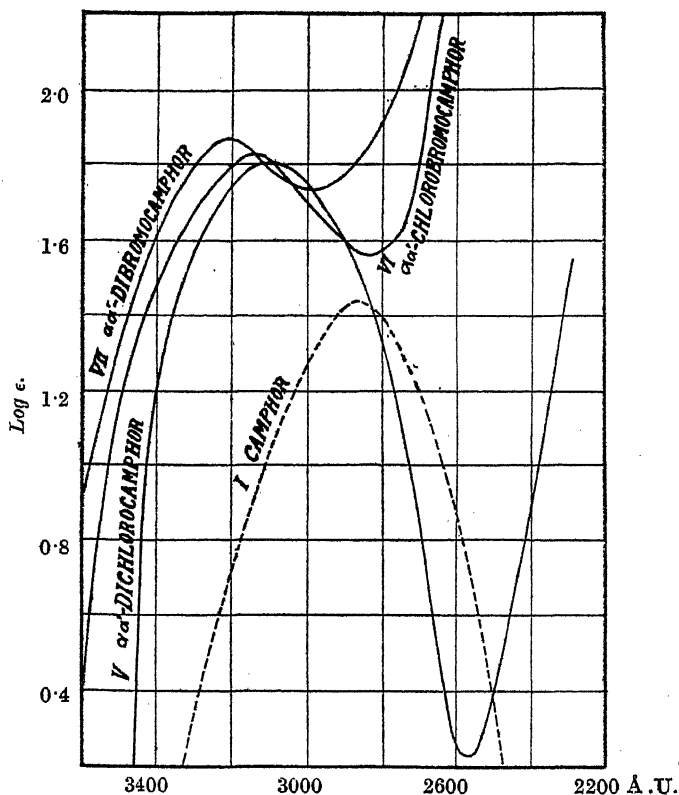
Molecular extinction coefficients of I camphor, II(a)  $\alpha$ -chlorocamphor, II(b)  $\alpha'$ -chlorocamphor, III(a)  $\alpha$ -bromocamphor, III(b)  $\alpha'$ -bromocamphor in cyclohexane.

compounds the progressive replacement of chlorine by bromine is accompanied by a progressive increase in the wave-length of the band, whilst the maximum extinction coefficient remains practically constant at a value midway between those recorded for a single atom of chlorine or bromine in the  $\alpha$ -position. On the other hand, a similar replacement of chlorine by bromine in the  $\alpha\beta$ -series (Fig. 3) produces a progressive increase in the value of the maximum



extinction coefficient, which is not accompanied by any marked change of wave-length. These two figures therefore recall, but in a much less striking form, the contrast between the optical effect of the two types of conjugation recorded in Part IV. In the  $\alpha\pi$ -series (Fig. 4), the principal contrast is between the  $\alpha$ -chloro- and the  $\alpha$ -bromo-compounds. Thus  $\alpha\pi$ -dichlorocamphor gives a band in

FIG. 2.

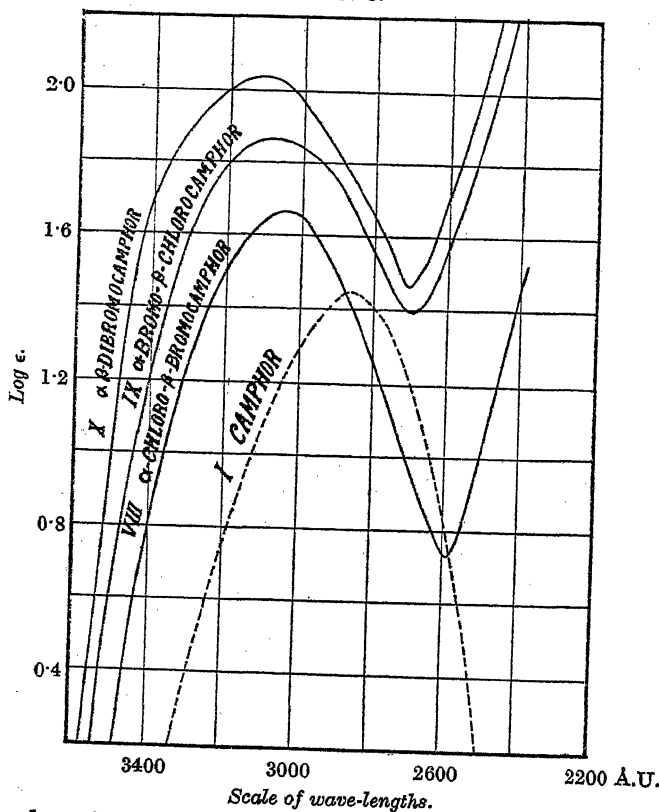


Molecular extinction coefficients of I camphor, V  $\alpha\alpha'$ -dichlorocamphor, VI  $\alpha\alpha'$ -chlorobromocamphor, VII  $\alpha\alpha'$ -dibromocamphor in cyclohexane.

very much the same position as in  $\alpha$ -chlorocamphor itself; and in the same way  $\alpha\pi$ - and  $\alpha'\pi$ -dibromocamphor (which give almost identical curves) and  $\pi$ -chloro- $\alpha$ -bromocamphor resemble  $\alpha$ -bromocamphor very closely, although the introduction of a halogen atom in the  $\pi$ -position appears to produce a minute increase both in the wave-length and in the maximum value of the extinction coefficient of the bromo-compounds.

(v) The influence of a sulphonic group in the  $\beta$ - or  $\pi$ -position is almost negligible, like that of a halogen atom in either of these positions. Thus in Reyckler's camphor- $\beta$ -sulphonic acid (Fig. 5) a small increase of intensity is balanced by a small decrease of wave-length, just as in  $\beta$ -bromocamphor (Fig. 7) a small decrease of intensity was balanced by a small increase of wave-length. Similar

FIG. 3.



Molecular extinction coefficients of I camphor, VIII  $\alpha$ -chloro- $\beta$ -bromocamphor, IX  $\alpha$ -bromo- $\beta$ -chlorocamphor, X  $\alpha$ - $\beta$ -dibromocamphor in cyclohexane.

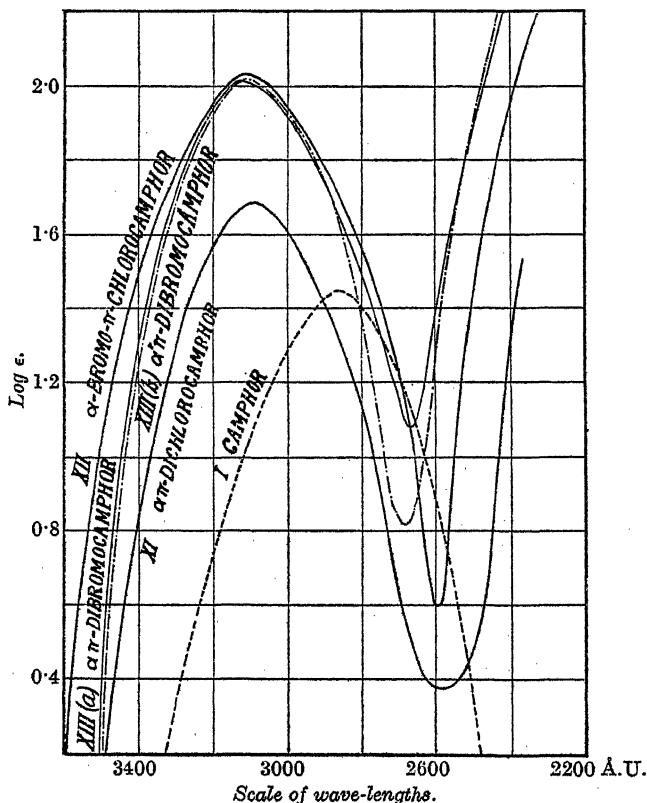
statements apply to the  $\alpha$ - $\beta$ - and  $\alpha$ - $\pi$ -chloro- and bromo-sulphonates, where the introduction of the sulphonic group produces only small changes in the wave-length and intensity of the band of  $\alpha$ -chloro- and  $\alpha$ -bromocamphor.

(b) *General Absorption.* For the purpose of comparing general absorptions, we have chosen, quite arbitrarily, a standard wave-length,  $\lambda = 2500$  Å.U., and a standard absorptive power,  $\log \epsilon =$

1.5, and have recorded in Table I the wave-length at which the standard absorptive power is attained, and the absorptive power at the standard wave-length. The principal experimental results are as follows :—

(i) We have obtained complete confirmation of the recent observation of Lowry and French (J., 1924, 125, 1924) that a solution of

FIG. 4.



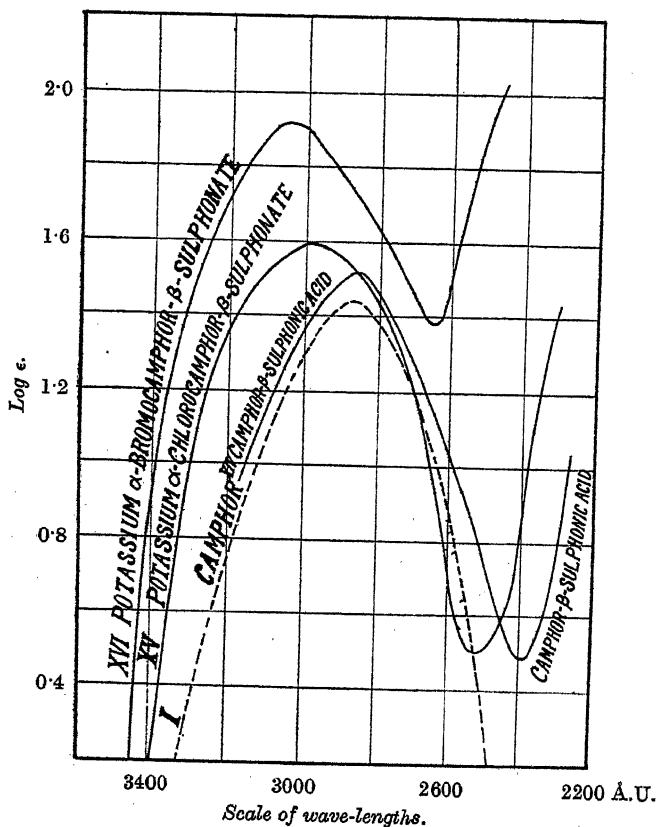
Molecular extinction coefficients of I camphor, XI  $\alpha\pi$ -dichlorocamphor, XII  $\alpha$ -bromo- $\pi$ -chlorocamphor, XIII (a)  $\alpha\pi$ -dibromocamphor, XIII (b)  $\alpha'\pi$ -dibromocamphor in cyclohexane.

camphor in *cyclohexane* shows no general absorption up to the limits of our present methods of measurement. It is therefore impossible to record the persistence of the band, except by stating that it must be greater than 1.7.\* It is indeed a noteworthy fact that, whereas

\* In the same way, V. Henri found (Ber., 1913, 36, 3627) that acetone shows no general absorption up to 2144 Å.U., although the band had already persisted through a range of 2.0 in log  $\epsilon$ , i.e., over a range of intensities of 100 : 1.

the earlier methods of measurement always indicated the existence of a real or fictitious general absorption in every solution that was examined, we have failed completely in our attempts to detect by the quantitative method any trace of a general absorption in camphor itself when dissolved in *cyclohexane*, although we have been able to

FIG. 5.



Molecular extinction coefficients of I camphor (in *cyclohexane*), XIV camphor- $\beta$ -sulphonic acid (in water), XV potassium  $\alpha$ -chlorocamphor- $\beta$ -sulphonate (in water), XVI potassium  $\alpha$ -bromocamphor- $\beta$ -sulphonate (in water).

reach the end of the band of selective absorption in all the twenty derivatives which were examined in the course of the present research, as well as in camphor itself when dissolved in alcohol (Lowry and French, *loc. cit.*). From the experimental point of view, it is a remarkable experience to find that a relatively strong solution of camphor, containing about 8 grams in 100 c.c., which extinguishes almost the whole of the ultra-violet spectrum from

3400 Å.U. onwards, becomes transparent again at about 2400 Å.U., and transmits with equal intensity all the remaining lines of the iron arc to 2327 Å.U.\*

(ii) After camphor, the smallest general absorption was observed in camphor- $\beta$ -sulphonic acid (Curve XIV), but, as the acid was examined in aqueous solution, the general absorption was easily observed, by reason of the exceptional transparency of the solvent. The minimum lies just beyond 2400 Å.U., but is followed by a very rapid increase, so that the general absorption was already almost level with the maximum of selective absorption (at  $\log \epsilon = 1.54$ ) when the last readings were taken at about 2327 Å.U., in the clear aqueous solution. Apart from camphor, this compound was the only one in which the standard wave-length,  $\lambda = 2500$  Å.U., selected for the comparison of general absorptions, fell within the limits of the band of selective absorption.

(iii) Although chlorine is not greatly inferior to bromine in its ability to intensify the selective absorption of camphor, it is relatively impotent in producing general absorption. Thus, apart from camphor and camphor- $\beta$ -sulphonic acid, the only compounds in which the absorptive power did not reach the standard value of 1.5 within the limits of our experiments were the  $\alpha$ - and  $\alpha'$ -chloro-camphors (Curves II, *a* and *b*). Again,  $\alpha\alpha'$ -dichlorocamphor (Curve V), where the growth of general absorption is much more rapid than in the monochlorocamphors, has an exceptionally deep minimum at  $\log \epsilon = 0.22$ ; and the persistence of the band,  $\log \epsilon (\text{max.}) - \log \epsilon (\text{min.}) = 1.60$ , is greater than in any compound of the series except camphor itself, where it exceeds 1.72 (Lowry and French, *loc. cit.*, p. 1925), and  $\alpha\pi$ -dichlorocamphor (Curve XI), where the general absorption only begins to be perceptible at a wave-length of about 2600 Å.U., after the band has attained a persistence of 1.68.

(iv) Bromine, on the other hand, which produces a strong general absorption even in  $\alpha$ -bromocamphor, becomes extremely efficient in this respect when reinforced by an atom of chlorine or bromine in the other  $\alpha$ -position. Thus, the general absorption at the standard wave-length of 2500 Å.U. *increases* from  $\log \epsilon = 1.83$  in  $\alpha$ -bromocamphor to 2.45 in  $\alpha\alpha'$ -chlorobromocamphor and to 2.86 in  $\alpha\alpha'$ -dibromocamphor. At the same time, as a result of the increase of general absorption, the persistence of the band *decreases* from 0.75 in  $\alpha$ -bromocamphor to 0.3 in  $\alpha\alpha'$ -chlorobromocamphor and to 0.1 in  $\alpha\alpha'$ -dibromocamphor (Fig. 2). The general absorption in  $\alpha\alpha'$ -di-

\* The fact that even this very "clean" band attains a width of 1000 Å.U. in solutions of only moderate concentration will explain why accurate measurements of rotatory dispersion can only be made for wave-lengths much greater than that of the crest of the band.

bromocamphor is indeed so great that at 2900 Å.U. it is already twice as strong as that corresponding with the maximum of the camphor band at the same wave-length. It is, therefore, only because the camphor band has been displaced by about 350 Å.U. in the direction of longer wave-lengths that the dibromo-derivative is able to exhibit a selective absorption at all: apart from this, nothing but a "step-out" would be observed in the curve.

(v) The reinforcement of the general absorption of  $\alpha$ -bromocamphor by a second halogen in the  $\beta$ -position is comparatively small. Thus the general absorption remains practically stationary on passing from  $\alpha$ -bromocamphor, where  $\log \epsilon = 1.83$  at 2500 Å.U., to  $\alpha\beta$ -bromochlorocamphor, where  $\log \epsilon = 1.90$ , although this number rises to 2.5 in  $\alpha\beta$ -dibromocamphor. In the case of the  $\pi$ -compounds,\* the general absorption actually *falls* from  $\log \epsilon = 1.83$  at 2500 Å.U. in  $\alpha$ -bromocamphor to 1.45 in  $\alpha\pi$ -bromochlorocamphor, and remains stationary at 1.83 in  $\alpha\pi$ -dibromocamphor. A sulphonic group in the  $\beta$  or  $\pi$ -position is also practically without influence in augmenting the general absorption of  $\alpha$ -bromocamphor, since the value of  $\log \epsilon$  is only increased from 1.83 at 2500 Å.U. in  $\alpha$ -bromocamphor to 1.90 in the two bromocamphorsulphonates.

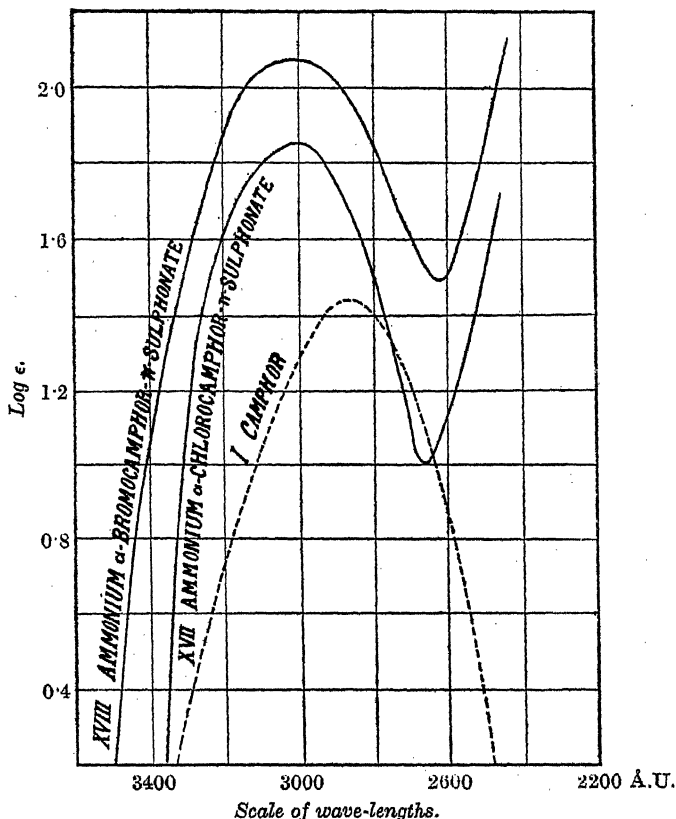
#### 4. *Superposition of Selective and General Absorption.*

In accordance with the usual behaviour of negative radicals, halogens in the contiguous  $\alpha$ -position have been found to augment the selective absorption of the ketonic group. Conversely, one must suppose that the ketonic group augments the power of the contiguous  $\alpha$ -halogen atom to develop a general absorption, just as it increases the readiness with which reduction or reverse substitution takes place. In these cases, therefore, any superposition of general and selective absorption by mere addition would be out of the question, since it would ignore the known mutual influence of the negative atoms. This mutual influence diminishes, however, as the distance between the negative atoms is increased; and in  $\beta$ -bromocamphor the band of selective absorption is very similar to that of camphor itself, showing that one of the two mutual influences (namely, that of the halogen upon the ketonic group, but not necessarily that of the ketonic group upon the halogen) has become almost negligible. We have therefore attempted to reproduce the absorption curve of  $\beta$ -bromocamphor by superposing the general absorption of a compound containing the group  $-\text{CH}_2\text{Br}$  (see Part VII) on the selective absorption of camphor itself. The general absorption of *one* molecular proportion of methyl bromide was found

\* Anomalies in the optical properties of the  $\pi$ -derivatives have already been noted and discussed (J. 1925, 127, 1504).

to be too small, whilst that of *half* a molecular proportion of methylene bromide or of ethylene bromide was too great, on account of the excessive mutual influence of the two halogens. Finally, by using a mixture of one molecular proportion of camphor with half a molecular proportion of trimethylene bromide (in which the two negative

FIG. 6.



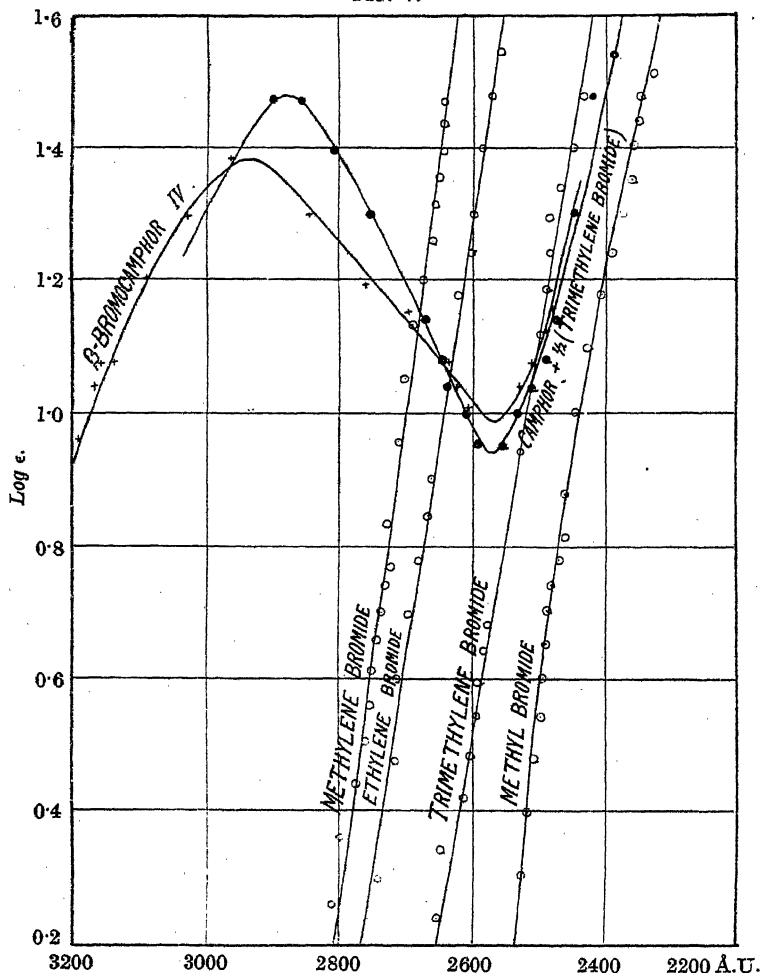
*Molecular extinction coefficients of I camphor in cyclohexane, XVII ammonium  $\alpha$ -chlorocamphor- $\pi$ -sulphonate, XVIII ammonium  $\alpha$ -bromocamphor- $\pi$ -sulphonate in water.*

atoms are separated by three intermediate atoms of carbon, just as in  $\beta$ -bromocamphor), we have obtained an absorption curve (Fig. 7) which pursues very much the same course as that of  $\beta$ -bromocamphor, although it is not identical with it. In this way the validity of the principle of superposition of general and selective absorptions appears to be sufficiently established, whilst the theory which assigns the selective absorption to the  $>\text{CO}$  group and the

general absorption to the  $\geq\text{C Br}$  group (see following paper) receives a direct experimental confirmation.

In addition to the absorption curve for  $\beta$ -bromocamphor, and the

FIG. 7.



Molecular extinction coefficients of IV  $\beta$ -bromocamphor in cyclohexane. Also of methyl, methylene, ethylene, and trimethylene bromide and of a solution of camphor with half a molecular proportion of trimethylene bromide in cyclohexane.

curve for a mixture of camphor and trimethylene bromide, Fig. 7 shows the curves of general absorption for solutions of methyl, methylene, ethylene and trimethylene bromides in cyclohexane, the curves plotted in Part VII being for solutions in alcohol. On account



of the narrower range of wave-lengths and intensities which it covers, this diagram was plotted on twice the scale of Figs. 1 to 6; it was therefore possible to insert, without overcrowding, all the experimental points on which the curves were based.

### 5. Auxochromic Influence of Alkyl Radicals and of Halogens.

Bielicki and Henri (*Ber.*, 1913, **46**, 3627) and Rice (*Proc. Roy. Soc.*, 1915, *A*, **91**, 76) have shown that the absorption band of acetone is displaced towards the visible region when the hydrogen atoms are replaced by alkyl groups. Thus according to Rice "the shifts obtained in the successive substitution of the three  $\alpha$ -hydrogen atoms are 23, 50, and 30 Å.U." for the first methyl, and the total shift of 103 units is doubled ( $\lambda = 2747 \rightarrow 2850 \rightarrow 2950$  Å.U.) when the three hydrogens of the second methyl group are also replaced. On the other hand, Henri finds that a shift in the same direction occurs when the whole methyl group is replaced by hydrogen, since aldehydes give a band of longer wave-length and smaller intensity than ketones, in addition to showing a much stronger general absorption.

In order to determine the influence of halogens (and of negative radicals generally) on the absorption spectra of the ketones, it is convenient to take camphor instead of acetone as the parent compound, since the liquid halogen derivatives of acetone are less easy to prepare and purify than the alkyl derivatives (which are easily synthesised) and are in every respect inferior to the analogous compounds of the camphor series, where crystalline products are available in large numbers, and with the substituent in four different positions, namely,  $\alpha$  or  $\alpha'$ ,  $\beta$  and  $\pi$ . It is a mere accident of nomenclature that in the  $\alpha$ - and  $\alpha'$ -derivatives of camphor the substituent is attached to a carbon atom in the " $\alpha$ " position relative to the ketonic group, and that in the case of the  $\beta$ -derivatives we can now assign the substituent to a methyl group of which the carbon atom is in a " $\beta$ " position relative to the ketonic group (Lowry and Burgess, *J.*, 1925, **127**, 279). In the  $\pi$ -compounds, the substituent is attached to a carbon atom in a " $\gamma$ " position relative to the ketonic group, although it can also be reached by a longer route which would make it a " $\delta$ " carbon atom. It is therefore possible, by working in the camphor series, to compare the effect on the selective absorption of the ketonic group of introducing a negative substituent in an  $\alpha$ -,  $\beta$ - or  $\gamma$ -position. The fact that the camphor nucleus is relatively complex is not a matter of great importance, since we have no reason for supposing that the influence of a negative group depends on the *shape* of the chain of atoms through which it is transmitted. It is, however, important to remember that there is

already evidence to show that the optical properties of the  $\pi$ -derivatives are sometimes abnormal (Richards and Lowry, J., 1925, 127, 1504).

With these facts in mind, the experimental data given above can be summarised by saying that, whilst the general absorption is influenced profoundly by the introduction of a negative group *in any position in the molecule*, the selective absorption is influenced strongly by a halogen atom only when this occupies a contiguous  $\alpha$ -position, the effect of a halogen or of a sulphonic group in the more distant  $\beta$ - and  $\gamma$  ( $\pi$ )-positions being negligible. Thus the increment for a single atom of bromine in the  $\alpha$ - or  $\alpha'$ -position is about 200 Å.U. (mean of 220, 240, 180, 150), and for a single atom of chlorine about 160 Å.U. (mean of 170, 180, 150, 130), when the other  $\alpha$ -position is occupied by hydrogen; and it is about 120 Å.U. for bromine and 50 Å.U., for chlorine, when the other  $\alpha$ -position is already occupied by a halogen. For a halogen in the  $\beta$ -position, the increments are -20, +50, +10, -20 Å.U. and for a halogen in the  $\pi$ -position, +30, +50, +20, -30 Å.U. A comparison with Rice's observations shows that the increments for two  $\alpha$ -atoms of chlorine, or for a single  $\alpha$ -atom of bromine, in camphor is already larger than for six  $\alpha$ -methyls in acetone.

### 6. Origin of the Ketonic Band.

At the time when the earlier observations of absorption spectra were made (J., 1909, 95, 807, 1340; 1910, 97, 899, 905) it was thought that selective absorption was due to an oscillation in the molecule of the same period as that of the absorbed light. The experiments then described showed, however, that the ketonic band could not be due to the "isorropesis" or intramolecular oscillation of a mobile hydrogen atom, since bands were developed by many compounds which were incapable of undergoing isomeric change in the manner suggested. The conclusion was therefore drawn that "the camphor band is evidently in some way a function of the ketonic group," but that "it is not at all easy to say in what way the group acts in promoting the formation of the band."

This problem has, however, been simplified considerably by recent developments in physical optics, which lead us to ascribe the absorption, not to an intramolecular vibration, but to the presence of a system which when activated by light can take up energy quanta of suitable magnitude. On inquiry amongst physicists, we find that the ultra-violet ketonic band cannot be attributed to activation of the nuclei of the carbon and oxygen atoms relatively to one another, since this would give bands in the infra-red region; nor can it be due to the ionisation of the unshared electrons of the oxygen

atom (*all* the carbon electrons are shared), since the ionisation potential for oxygen corresponds with a wave-length far out in the Schumann region. The ketonic band can therefore only be attributed to an activation of the valency electrons of the double bond which forms the link between carbon and oxygen.

These valency electrons differ from the others in being simultaneously under the control of two nuclei, A and B. They can therefore be raised to a higher energy level relatively to A, or to B, or to A and B simultaneously. If A is carbon and B is oxygen (or in general if A is a less "negative" element than B), it will be easier to activate the valency electrons relatively to A than relatively to B. The effect will be to produce a "polar activation" of the double bond, since the valency electrons which absorb the light will be displaced from carbon towards oxygen, a process which (if continued far enough) would culminate in the ionisation of one link of the bond, and the conversion of the "non-polar" into a "semi-polar" double bond, as indicated by the scheme  $>C=O \rightleftharpoons >\overset{+}{C}-\bar{O}$ .

The theory of polar activation, now used to explain the absorption of light by the unsaturated carbonyl radical, corresponds closely with the explanation given by Norrish (in Part III of this series of papers, J., 1923, 123, 3006) of the arrest of the interaction of ethylene with bromine or chlorine, when enclosed in a vessel lined with paraffin wax, *i.e.*, that the interaction depends on a "polar activation" of the olefine and halogen, which can only be brought about at a polar surface. It should also be noted that, whilst semi-polar double bonds are permanent in the systems  $>SO$ ,  $\geq NO$ , and  $\geq PO$ , they are not stable in  $>C=C<$  or  $>C=O$  (Sugden, J., 1925, 127, 1525); they are, therefore, available as unstable or activated forms of the molecule in order to account for phenomena such as those discussed above.

The views now set out in reference to the utilisation of the energy absorbed by double bonds in unsaturated compounds could obviously be extended to single bonds; but since these are usually much more stable than double bonds, the quanta of energy required to activate them must be much larger, and the wave-lengths much smaller, than in the case of the ketonic band, corresponding, for instance, with a frequency in the Schumann region of the spectrum. Since this region is still inaccessible to our present methods of investigation of absorption spectra, saturated compounds generally give rise only to "general absorption."

## 7. Summary.

(a) Quantitative data are given for the general and selective absorption of twenty halogen and sulphonic derivatives of camphor.

(b) Halogen atoms in the  $\alpha$ -position intensify both the general and the selective absorption of camphor; but halogen atoms and sulphonic groups in the  $\beta$ - or  $\pi$ -position are relatively impotent in increasing the selective absorption of the ketone, although they may contribute substantially to its general absorption.

(c) The origin of the ketonic band is discussed.

We wish to acknowledge our indebtedness to the University of Wales for a Fellowship Grant which has enabled one of us (G.O.) to take part in this work.

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### LXXXIV.—*Studies of Valency. Part VI. General and Selective Absorption of Halogen Derivatives of Methane. The Origin of General Absorption.*

By THOMAS MARTIN LOWRY and ROSE RACHEL SASS.

#### 1. *Purpose of the Experiments.*

(a) THE observations described in the preceding paper created the impression that, just as the selective absorption of the ketones can be attributed to some form of polar activation or incipient ionisation of the *double* bond of the carbonyl group, so their general absorption might be attributed to the activation or incipient ionisation of a *single* bond, e.g., between carbon and hydrogen or between carbon and a halogen. In camphor itself, the single bonds appear to be so strong that they can only be activated by, and can therefore only absorb, light of very high frequency; the corresponding maximum of "general" absorption is therefore so remote that even the foot of the band cannot be detected at a wave-length of 2400 Å.U. On the other hand, in  $\alpha\alpha'$ -dibromocamphor (where the bonds between carbon and bromine are so weak that the compound acts as an oxidising agent) the general absorption is so strong that it almost covers up the selective absorption. The increase of absorptive power is indeed so rapid as to indicate that it must reach a maximum at a wave-length not far beyond the limits of our experiments. We therefore formed the opinion that, just as the double bond of the carbonyl group produces a characteristic absorption at about 2700 Å.U., so the single bond between carbon and bromine might have a characteristic absorption at some shorter wave-length; and that just as the maximum of the ketonic band of camphor can be shifted to the extent of some 350 Å.U. under the influence of contigu-

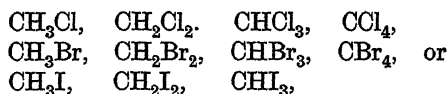
ous negative atoms, so the band of general absorption might be shifted through some hundreds of Ångström units in the direction of longer wave-lengths, as a result of the weakening of the single bond under the influence of contiguous negative atoms. This view, which served to explain the close analogy between the influence of the halogens on the selective and on the general absorption of the halogen derivatives of camphor, had the advantage that it could be tested by direct experiments on a much simpler series of compounds, and in this way it led to the experiments on the general and selective absorption of the halogen derivatives of methane, which form the subject of the present paper.

(b) In the experiments on general absorption advantage was taken of the fact that the introduction, first of the sector-photometer and then of the ultra-violet spectrophotometer, has made it possible to measure the molecular extinction coefficients of a solution in the ultra-violet region, and so to make an exact quantitative comparison of the general absorptions of a series of substances. Previous observations, in which the older qualitative methods were used (Crymble, Stewart, and Wright, *Ber.*, 1910, 43, 1183; Massol and Faucon, *Compt. rend.*, 1917, 164, 813), had given numerical values only for the characteristic wave-lengths of the iodo-compounds, which are the only ones to show a selective absorption in the accessible ultra-violet region.

(c) On the supposition that a marked general absorption could be produced by the incipient ionisation of a weak single bond between carbon and a halogen we anticipated :

(i) That the general absorption would increase progressively in the series  $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ , since the bond between carbon and fluorine is known to be extremely strong, whilst the bond between carbon and iodine is so weak that it can be ionised quite readily, *e.g.*, in the formation of a methiodide from an alkyl iodide and a nitrogenous base, or in the interaction between methyl iodide and silver nitrate in the Zeisel method of estimating methoxyl groups.

(ii) That the general absorption would increase in series such as :



since the accumulation of negative atoms would tend to weaken the bond between the carbon and the halogen, and so bring the crest of the band nearer to the accessible ultra-violet region. These anticipations have been fulfilled, as can be seen from the following summary of the experimental results.

## 2. Summary of Experimental Results.

The experimental data in reference to the halogen derivatives of methane are shown in Fig. 1, and are summarised in Table I.

TABLE I.

*Absorption Spectra of Alcoholic Solutions of Halogen Derivatives of Methane.*

Formula of substance.	Wave-lengths for integral values of log $\epsilon$ .					
	log $\epsilon$ = 0.0.	1.0.	2.0.	3.0.	4.0.	5.0.
CHCl <sub>3</sub>	2320					
CCl <sub>4</sub>	2700	2500	2360			
CH <sub>3</sub> Br	2640	2360				
CH <sub>2</sub> Br <sub>2</sub>	2900	2700	2560	2300		
CHBr <sub>3</sub>	—	3000	2900	2400		
CBr <sub>4</sub>	—	3600	3300	2600		
CH <sub>3</sub> I	—	3000	2900			
CH <sub>2</sub> I <sub>2</sub>	3900	3720	3600	3200		
CHI <sub>3</sub>	—	—	4500	3900	2200	

Position of maxima.						
(a) Lowry and Sass.		(b) Crymble, Stewart, and Wright.		(c) Massol and Faucon.		
	Å.U.					
I <sub>2</sub>	{ log $\epsilon$ = 2.7 at 4770 log $\epsilon$ = 3.3 at 2900 }	4800	—	3030	—	4700 3500 2880 —
CH <sub>3</sub> I	log $\epsilon$ = 2.7 at 2600	—	—	2570	—	— — — 2500
CH <sub>2</sub> I <sub>2</sub>	log $\epsilon$ = 3.1 at 2960	—	—	3030	—	— — 2880 —
CHI <sub>3</sub>	log $\epsilon$ = 3.5 at 3450, 2940	—	3570	3030	—	— 3350 2880 —
Cl <sub>2</sub>						— 3450 2880 —
KI <sub>3</sub>	log $\epsilon$ = 3.9 at 3550, 2900	—	3570	3030	—	

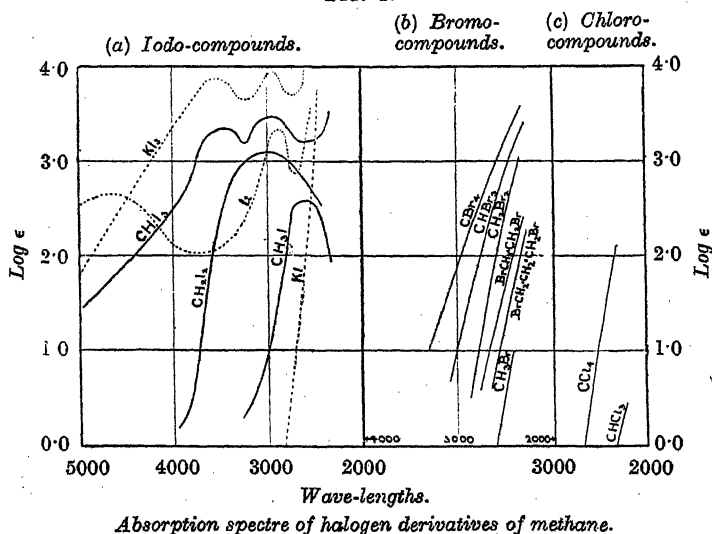
(i) The data recorded above show that the absorptive power of the chlorine compounds is very slight. Thus even chloroform only produces a measurable absorption at high concentrations and short wave-lengths, *e.g.*, the value of log  $\epsilon$  at 2400 Å.U. is only -1.0. Carbon tetrachloride, however, develops a marked absorptive power at 2700 Å.U., where log  $\epsilon$  = 0.0, and gives rise to a well-defined curve of general absorption (Fig. 1, c).

(ii) Just as  $\alpha\alpha'$ -dibromocamphor gives rise to a much greater general absorption than  $\alpha\alpha'$ -dichlorocamphor, so the bromoderivatives of methane are much more absorptive than the corresponding chloro-compounds. Thus methyl bromide is nearly as absorptive as carbon tetrachloride; and the general absorption becomes increasingly strong in the series CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, CBr<sub>4</sub> (Fig. 1, b), until in the last compound the foot of the band begins to approach the violet end of the visible spectrum. It is noteworthy that the general absorption of  $\beta$ -bromocamphor, where the distance between the bromine atom and the oxygen of the ketonic group is sufficiently great to prevent the two negative radicals from influencing each other to any large extent, is very similar to that of methyl

bromide; thus the molecular extinction coefficient, which rises to  $\log \epsilon = 1.1$  at 2500 Å.U. in  $\beta$ -bromocamphor, reaches the same value at 2400 Å.U. in methyl bromide. This result is in harmony with the view that in both cases the weak bond which gives rise to the general absorption is the bond between carbon and bromine.

(iii) Conclusive evidence that the general absorption of the halogen derivatives of methane is due to a band of short wave-length, and that this wave-length can be increased by weakening the bond which links the halogen to the carbon, was obtained from the study of the iodides of the series  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$ ,  $\text{CHI}_3$ . In this series, although we only expected to find an enhanced "general absorption,"

FIG. 1.



definite bands are in fact developed (Crymble, Stewart, and Wright, *Ber.*, 1910, **43**, 1183; Massol and Faucon, *Compt. rend.*, 1917, **164**, 813). Up to a certain point the extinction coefficients of methyl iodide are almost identical with those of bromoform, *viz.*,  $\log \epsilon = 1.0$  at 3000 Å.U. and 2.0 at 2800 Å.U.; but the curve for the iodide, instead of rising progressively to  $\log \epsilon = 3.0$  at 2400 Å.U., reaches a maximum,  $\log \epsilon = 2.6$  at 2600 Å.U., and then falls again to  $\log \epsilon = 2.0$  at 2327 Å.U. (Fig. 1, a).

(iv) The absorption band, which thus makes its appearance for the first time in methyl iodide, develops progressively in the series  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{I}_2$ ,  $\text{CHI}_3$ , until, in the case of iodoform, the foot of the band extends half-way across the visible spectrum. The visible colour of this compound, however, unlike that of *p*-benzo-

quinone, is still due to a selective absorption in the ultra-violet. The appearance of a general absorption beyond the band is a novel feature, which was seen for the first time in iodoform; but no great significance appears to attach to it, since it merely suggests the existence of a reserve of bands of shorter wave-length, which can be shifted towards the accessible ultra violet region by the accumulation of negative atoms.

(v) The most interesting feature of the iodoform curve is the division of the crest of the band into two maxima,  $\log \epsilon = 3.5$  at 3450 and 2940 Å.U., separated by a shallow minimum. It is not certain, however, whether even this should be regarded as an entirely abrupt development, since the band becomes progressively wider on passing from methyl iodide to methylene iodide and then to iodoform, although a careful examination failed to reveal any similar subdivision of the crest of the band in methylene iodide. The general form and position of the curves certainly suggest that we are dealing with the same band throughout, and that, although the second and third atoms of iodine may reinforce and develop the band, they are not needed in order to initiate it. It is, however, equally clear that the striking development of the band in methylene iodide and in iodoform reveals the influence of certain novel factors, which are not present in the simple alkyl iodides and are sufficiently important to form the subject of a separate discussion.

### 3. *Absorption Spectra of Iodine, Potassium Iodide, and Potassium Tri-iodide.*

In view of the qualitative comparisons which earlier workers have made between the absorption spectra of the iodo-derivatives of methane and those of solutions of iodine in alcohol and in aqueous potassium iodide, we have thought it desirable to include these solutions in our series of quantitative measurements. The results are shown in Fig. 1, *a*, together with a curve of general absorption of potassium iodide. They have also been included in Table I. The general conclusions are as follows:

(a) Although visible colour is developed more readily in compounds of iodine than in those of the other halogens, so many colourless compounds of iodine are known that one must suppose its chromophoric properties to be like those of oxygen, which depend on the mode of combination of the element, rather than like those of chromium or cobalt, where the elements seem to be almost incapable of yielding colourless derivatives. It is, therefore, very doubtful whether Massol and Faucon were justified, after recording the existence of three bands at 4700, 3500, and 2880 Å.U. in an alcoholic solution of iodine, in identifying these same bands in the



absorption spectra of the iodo-derivatives of methane. A theoretical objection to this method of treatment is found in the fact that, according to the conventional view, the atoms of iodine in an alcoholic solution are linked only by iodine-iodine bonds, whilst in the iodo-derivatives of methane all the atoms of iodine are held by carbon-iodine bonds. There is, therefore, no obvious basis for an identity of characteristic frequency, unless it arises from the inherent properties of the iodine atom or molecule; and the former alternative at least is ruled out by the fact that the frequency of the band in methyl iodide (2600 Å.U.) is so far different from that of the iodine bands that Massol and Faucon did not attempt any identification in this case. On the experimental side, this identification is limited by the fact that the band at 4800 Å.U., which imparts a visible colour to the alcoholic solution of iodine, is not reproduced in any of the derivatives, the colour of which is invariably due to the extension into the visible spectrum of the foot of an ultra-violet band. The second band at 3500 Å.U. can also be omitted from the discussion, since it is not recorded by Crymble, Stewart, and Wright, and no trace of it can be found on the quantitative curves which we have plotted in Fig. 1, *a*. It is therefore only the third band, at 2900 Å.U., that is available for the purpose of identification.

A band at 2900 Å.U. occurs in the absorption spectrum of iodine in aqueous potassium iodide, as well as of iodine in alcohol; but it is accompanied by a second band at 3500 Å.U., which is of much shorter wave-length than the visible band at 4770 Å.U. of the alcoholic solution. It is, therefore, impossible to attribute the selective absorption at 2900 Å.U. to the presence of free iodine in the aqueous iodide solution. If, therefore, the band is really the same in the two cases, it must be ascribed to some identical type of bond between the atoms of iodine, a conclusion against which no theoretical objection can be urged.

We have already seen that the wave-length of the band in methyl iodide is less than in elementary iodine; but in methylene iodide it is approximately equal to it. Since ethylene iodide gives a band of the same frequency as methyl iodide, although of rather greater intensity, Crymble, Stewart, and Wright attribute the methylene iodide band to the juxtaposition of two atoms of iodine in the same molecule, *i.e.*, they suggest that  $\text{I}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{I}$  gives the same band as  $\text{I}-\text{I}$ , but that  $\text{I}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{I}$  behaves like  $-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{I}$ . Our own measurements indicate, however, that the band in methylene iodide reaches a maximum at 2960 Å.U., and is definitely of lower frequency than the iodine band at 2900 Å.U. It is, moreover, quite different in appearance, and could only be identified with the iodine band on the

assumption that it was really a double band, of which one component was identical with one of the bands of elementary iodine. It is therefore only in iodoform that any real identification is possible.\*

(b) Whilst Massol and Faucon attempt (perhaps somewhat unreasonably) to identify the bands of elementary iodine with those of its derivatives, Crymble, Stewart, and Wright associate together the spectra of potassium tri-iodide and iodoform. This identification appeared at first sight to be at least equally unreasonable, since the colour of the tri-iodide is always attributed to the negative ion  $I_3^-$ , which (like iodine itself) can only contain iodine-iodine bonds, whilst in iodoform the three atoms of iodine have always been regarded as linked independently to a central atom of carbon. Before accepting so remote an identification, therefore, we regarded it as essential to plot quantitative absorption curves for the two substances. The result has been to establish a degree of resemblance which is even closer than that shown by the qualitative curves. Thus (i) each spectrum includes two bands, and only two, in the accessible range of the spectrum.

(ii) The foot of the band of longer wave-length extends in each case into the visible spectrum and gives rise to visible colour.

(iii) In the same way, the band of shorter wave-length is followed almost immediately by a strong general absorption.

(iv) The persistence of the band of shorter wave-length is thereby limited to about 0.25 in both compounds.

(v) The two crests are of similar wave-length, namely, 3500 and 2900 Å.U. for potassium tri-iodide and 3450 and 2940 for iodoform.

(vi) In both cases the two crests are of equal intensity.

(vii) They are also separated by a shallow minimum which limits the persistence of the band of longer wave-length to about 0.25 in both cases.

(viii) Finally, the intensities of the bands on the absolute scale, although not identical, are almost the same in the two cases, namely  $\log \epsilon = 3.5$  for iodoform and 3.9 for potassium tri-iodide.

These eight points of agreement, which appear to us to be far beyond the possibilities of a mere coincidence, point to the existence of some definite similarity of structure between the two compounds. No such similarity is indicated, however, by any of the conventional formulæ. Thus, the most plausible formula for the  $I_3^-$  ion is perhaps

\* Carbon tetraiodide is so unstable in alcoholic solution that it was not investigated by Crymble, Stewart, and Wright, nor by ourselves; we cannot therefore say what weight should be attached to the statement of Massol and Faucon that it gives the same bands as iodoform.

one which represents it as the analogue of the  $\text{HF}_2^-$  ion, *e.g.*,  $\overset{+}{\text{K}}[\overset{+}{\text{I}}\overset{+}{\text{I}}\overset{+}{\text{I}}]$  (compare  $\overset{+}{\text{K}}[\overset{+}{\text{F}}\overset{+}{\text{F}}\overset{+}{\text{F}}]$ ); but the formula of iodoform cannot be made to conform to this pattern, since it has always been assumed that the three atoms of iodine are linked directly to carbon and not to one another. The stricter rules of the electronic theory of valency forbid, in an even more emphatic manner than before, any tampering with these formulæ, *e.g.*, by assigning a higher covalency to iodine, and thus superposing a ring structure on the traditional tetrahedron. We can therefore only conclude that our present theories of valency are inadequate to express certain features of molecular structure which may become of predominant importance in cases such as that now under consideration. It appears, indeed, as if both molecules were dominated by a cluster or ring of three contiguous iodine atoms, just as (according to W. L. Bragg's recent determinations) the crystal structure of most of the oxy-salts and of many of the metallic oxides is dominated by clusters of contiguous oxygen atoms, leaving the co-ordinating atom to occupy a mere cavity between the oxygens. This picture, from which all traces of the bonds between the atoms have been erased, is admittedly unconventional, but it appears to be the only one which gives any clue to the origin of the amazing similarity of the two absorption spectra.

#### 4. Summary and Conclusions.

(a) The general absorption of the chloro- and bromo-derivatives of methane increases progressively from chloroform to carbon tetrabromide. Methyl iodide, however, produces a band which becomes more intense and of longer wave-length on passing to methylene iodide and to iodoform, where the crest of the band is finally resolved into two maxima.

(b) The ultra-violet absorption band of methyl iodide cannot be explained by any of the older theories of colour, but finds a simple explanation in the relative weakness of the bond between carbon and iodine, and the consequent smallness of the quanta of energy that are required to activate it. The suggestion is therefore made that the general absorption of the halogen derivatives of camphor and of methane, and the intensification of the general absorption by an accumulation of contiguous negative atoms, is due to the activation or incipient ionisation of a single bond, just as the ketonic band of camphor may be attributed to the activation or incipient ionisation of the double bond of the carbonyl group.

(c) There is a close resemblance between the absorption spectra of iodoform and of potassium tri-iodide, which is not accounted for by the formulæ commonly assigned to these compounds, and appears

to be beyond the scope of our present theories of valency. It may, however, be due to the presence of three contiguous atoms of iodine in the space models of the two compounds.

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### LXXXV.—*The Equivalent Conductivity of Solutions of Sodium Hydroxide and the Mobility of the Hydroxyl Ion.*

By HUMPHREY RIVAZ RAIKES, ALBERT FREDERICK YORKE, and  
FREDERICK KENNETH EWART.

THE object of the work detailed in this paper was to make use of the very pure water obtainable from stills of the type described by Bourdillon (J., 1913, 103, 791) for determining the value of the mobility of the hydroxyl ion.

It has long been recognised that the chief impurity in conductivity water is carbon dioxide. Present as it is in extremely small quantities, its effect on the conductivity of solutions of salts and to a less degree of acids may well be regarded as negligible and the true value of the conductivity is obtained from the observed value by subtracting a "water-correction."

With hydroxides, however, the case is quite different, since slow-moving carbonate ions are substituted for mobile hydroxyl ions and in very dilute solution the conductivity is that of a carbonate and not that of a hydroxide. The observed values will thus be less than the true values and if anything a correction should be added instead of subtracted.\* As, however, the determination of the value of this correction is not a simple matter, our method has been to use only water of the highest purity and to regard the whole conductivity as being due to the hydroxide.

The still used was a slightly modified Bourdillon still. It delivered, in quantity, water of specific conductivity 0.06—0.07 gemmho, and in the best experiments this had not increased beyond 0.09 gemmho after the water had been transferred to the conductivity cell.

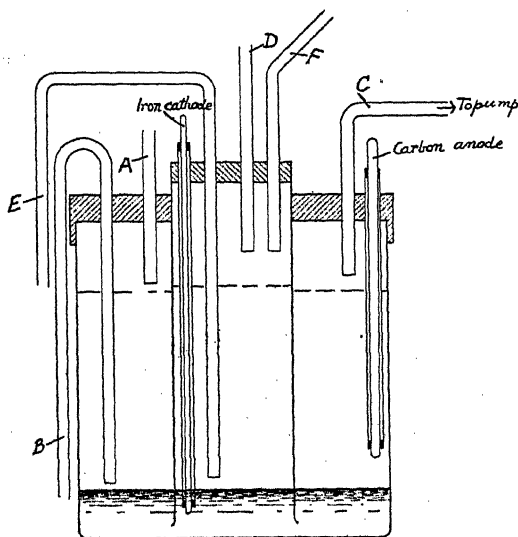
\* Mr. W. F. K. Wynne-Jones has very kindly examined our figures and in one run where water of 0.599 gemmho purity was used and in which the equivalent conductivity showed a maximum at a concentration of 0.0007 mol. per litre he has shown that the application of a correction based on the assumption that the conductivity of the water was due to carbon dioxide brings the values obtained into close agreement with those found by us in water of a high degree of purity.

## EXPERIMENTAL.

*Preparation of Sodium Hydroxide Solutions.*—The chief methods available for the preparation of pure aqueous sodium hydroxide are (i) the action of water on metallic sodium; (ii) methods involving the precipitation of the carbonate present in ordinary sodium hydroxide by means of a barium or calcium salt; (iii) the electrolysis of an aqueous solution of a sodium salt.

In the first method, the difficulty is to get rid of the scale of carbonate on the surface of the metal before submitting it to the action of water.

FIG. 1.



*Apparatus for the preparation of sodium hydroxide solutions.*

In the second method, it is impossible to avoid the presence in the final product of either barium or calcium. Noyes states (*Pub. Carnegie Inst.*, 1907, No. 63) that his final product contained at least 0.1% of barium sulphate.

A very pure product may be obtained, however, by the third method.

A method somewhat similar to ours for obtaining aqueous sodium hydroxide free from carbonate has been described by Jorissen and Filippo (*Chem. Weekblad*, 1909, 6, 145).

*Description of Apparatus.*—The cell (Fig. 1) consisted of an outer vessel of common glass about a litre in capacity, carrying a wide glass tube of about 200 c.c. capacity which was made the cathode

compartment. The tube was at first of Jena glass and later of Pyrex glass; no difference in the purity of the final product could be detected. All the glass tubing used was boro-silicate and was well steamed before being made up. The bottom of the cell was covered to the depth of about an inch with mercury, previously distilled in a vacuum.

A tightly fitting wooden cap in the outer vessel carried the cathode compartment and other accessories. The lower end of the cathode compartment dipped well below the surface of the mercury, but did not touch the bottom of the outer vessel. A tightly fitting cork in the top of the cathode compartment itself carried the accessories necessary in this compartment.

The anode consisted of a carbon rod, which was rather rapidly attacked by chlorine; it was protected as far as possible by means of a glass tube, and arranged so that its end was about 1 inch above the mercury surface.

The cathode was of iron protected by a sheath of borosilicate glass tubing; its lower end dipped into the mercury and the iron never came into contact with the solution in the cathode compartment.

At first the whole apparatus was arranged so that it could be rocked gently in order to facilitate the passage of the sodium amalgam into the cathode compartment. This rocking was, however, found to be unnecessary and was abandoned.

The current used was about 2.3 amps. when the cell could be watched, but when it had to be left this was reduced to 1.2 amps. in order to avoid the risk of heating.

*Procedure when Working the Cell.*—The mercury having been run into the cell, the cap was placed in position and sealed on. As an additional precaution, the whole of the outside of the cap was covered with a layer of high melting-point paraffin-wax.

The cathode compartment was washed from five to six times with fairly good conductivity water; the water being run in through *D* and syphoned out through *E*.

A normal solution of sodium chloride (Merck) made up with water of about 0.5 gemmho conductivity was run into the anode compartment through the tube *A*, so that the level of the liquid was about an inch below the end of *C*; the tube *A* was then fitted with a soda-lime tube.

A current of dry air, free from carbon dioxide and ammonia, was next passed through the cathode compartment, *via* the tube *F*, the tubes *D* and *E* during this operation carrying soda-lime tubes; after this, the tube *F* was connected to a soda-lime tube.

Finally, about 200 c.c. of pure water (0.3 gemmho conductivity)

were run into the cathode compartment through the tube *D*, which was connected to the flask delivering the water, so that at no time did the latter come into contact with the atmosphere. The tubes *D* and *E* were then closed.

The current was now switched on, the hydrogen evolved at the cathode escaping through the soda-lime tube connected with *F*, and the chlorine being drawn off through *C* by means of a water pump; it was found necessary to connect the tube *A* to the air (through a soda-lime tube) in order to prevent a reduction of pressure taking place in the anode chamber, and consequent passage of the cathode liquid into the anode compartment. The exhausted brine was syphoned off through *B*.

Care was taken to keep the temperature of the cell as low as possible during the reaction, in order to prevent the solution of silica. The temperature at no time rose above 40° and was usually kept between 25° and 30°.

After the current had passed for about 6 hours, some of the sodium hydroxide in the cathode compartment was drawn off, and its strength roughly estimated. The solutions eventually used varied from *N*/10 to *N*. The main quantity of solution was then transferred by suction to a Jena glass flask which had been previously steamed and filled with pure air.

Thus the sodium hydroxide solution never came into contact with the air of the room at any time during its preparation. The solution was stored in this flask until required for a dilution, but was rarely kept for more than 3 days before being so used.

*Purity and Analysis of the Sodium Hydroxide Solutions.*—The sodium hydroxide prepared as above was invariably tested for chlorine and carbon dioxide, the former by the nephelometric method of Richards (*Amer. Chem. J.*, 1904, **31**, 235; 1906, **35**, 99), and the latter by mixing with baryta in the nephelometer by a method which enabled the solutions to be compared without any risk of contamination by carbon dioxide. The solutions never showed a greater cloudiness than a clear solution of baryta which was used as standard. Chlorine was always absent. The analysis of the solutions was carried out by means of weight titrations against hydrochloric acid, with methyl-red as indicator. The analyses were always done in triplicate and never differed by more than 1 part in 10,000. The hydrochloric acid was purified and estimated by Richards's method (*J. Amer. Chem. Soc.*, 1905, **27**, 459). Three analyses of each sample were made and the results agreed to 1 part in 20,000.

The weights used were standardised by Richards's method (*J. Amer. Chem. Soc.*, 1900, **22**, 144) and the appropriate vacuum correction was always applied. The densities of the sodium

hydroxide and hydrochloric acid solutions were taken from Landolt and Bornstein's tables.

*The Conductivity Measurements.*—The cell used was one designed by Hartley and Barrett and will be described in a future publication. It consisted essentially of a 1500 c.c. Jena glass beaker, to the top of which was cemented a brass ring. To this ring was attached by means of screws a silver-plated brass cover which carried the electrodes, a stirrer, and a thermometer, and was provided with two openings through one of which a stream of pure air could be passed, whilst the tip of the weight pipette was inserted through the other. These openings could be closed at will. The electrodes were coated with platinum black.

All the resistances were calibrated against Wolff standards which had been recently restandardised at the National Physical Laboratory.

The cell constant, determined in the manner described by Frazer and Hartley (*Proc. Roy. Soc.*, 1925, A, 109, 355), had the value 0.1367, identical with the value obtained by Hartley and Barrett in 1909.

*The Thermostat.*—The temperature variation of the bath was never more than  $\pm 0.01^\circ$  and for most of the runs it did not exceed  $\pm 0.005^\circ$ .

*The Weight Pipette.*—The weight pipette used for adding the solution to the cell was provided with a filling arrangement which effectually prevented the contamination of the solution by the carbon dioxide of the air.

A run was carried out by adding weighed portions of stock solution to the solvent in the cell.

*Cleaning and Drying the Cell.*—After each run the cell was rinsed out several times with pure water, and the electrodes, thermometer, and stirrer were cleaned by means of a stream of water. The cell was then filled with about a litre of pure water, the top placed in position, and the stirrer set going for several hours. The water was changed at least once a day and stirred. When the cell was required for a run, the beaker was inverted and allowed to drain for about 6 hours; the rest of the cell was also drained. For the first two runs the beaker was finally dried by means of filter-paper; the thermometer and stirrer were dried in a similar manner. The electrodes were dried by just touching their edges with filter-paper.

It was found later that the water was of better quality if the beaker was not wiped, but if, after draining, the top was placed in position and a current of dry air passed through it for several hours, the stirrer being rotated in order to keep the air circulating. This was found to be a very effective method of drying.



*The Results.*—In all, seven runs were carried out at 18° and two at 10°. The figures in Tables I and II show that even in the best water the equivalent conductivity fell off in solutions less concentrated than  $N/1000$ . In some of the earlier runs the values obtained were quite untrustworthy.

All concentrations are given in gram-molecules per litre at the temperature of experiment ( $\text{NaOH} = 40$ ).

TABLE I.

## Equivalent Conductivity of Sodium Hydroxide at 18°.

Uncorrected for solvent conductivity.

Run H. 31/5/1922.  $T = 18^\circ \pm 0.005^\circ$ . Water 0.086 gemmho.

Conc. $\times 10^4$	0.266	0.576	0.889	2.45	7.24	17.87	29.9
A .....	171.8	185.0	189.0	200.7	205.0	208.0	208.0

Run K. 12/6/1922.  $T = 18^\circ \pm 0.005^\circ$ . Water 0.084 gemmho.

Conc. $\times 10^4$	2.54	5.85	11.28	22.5	48.7	99.5	170	319
A .....	208.3	211.4	214.4	213.6	211.4	209.5	207.6	203.8

Run L. 20/6/1922.  $T = 18^\circ \pm 0.005^\circ$ . Water 0.087 gemmho.

Conc. $\times 10^4$	10.5	22.3	41.2	76.4	158	277	545
A .....	215.0	213.7	212.0	210.1	207.9	204.9	198.1

TABLE II.

## Equivalent Conductivity of Sodium Hydroxide at 10°.

Uncorrected for solvent conductivity.

Run D. 29/4/1922.  $T = 10^\circ \pm 0.01^\circ$ . Water 0.082 gemmho.

Conc. $\times 10^4$ ...	0.431	1.26	8.42	17.6	33.1
A .....	152.4	169.1	178.3	178.6	178.0

Run M. 22/6/1922.  $T = 10^\circ \pm 0.01^\circ$ . Water 0.089 gemmho.

Conc. $\times 10^4$ ...	9.74	18.9	36.7	73.5	144	285
A .....	179.2	178.2	177.0	176.6	175.1	173.0

Fig. 2 gives the graph of equivalent conductivity plotted against the square root of the concentration, and it will be seen that for solutions more concentrated than  $N/1000$  the points lie on straight lines up to a concentration of  $N/30$ . The equations to these lines are :

$$\begin{aligned} &\text{at } 18^\circ, \Lambda_{18} = 217 - 75.7\sqrt{c} \\ &\text{and at } 10^\circ, \Lambda_{10} = 180.2 - 44.2\sqrt{c}, \end{aligned}$$

$c$  being the concentration of the solution in gram-molecules per litre at the temperature of experiment.

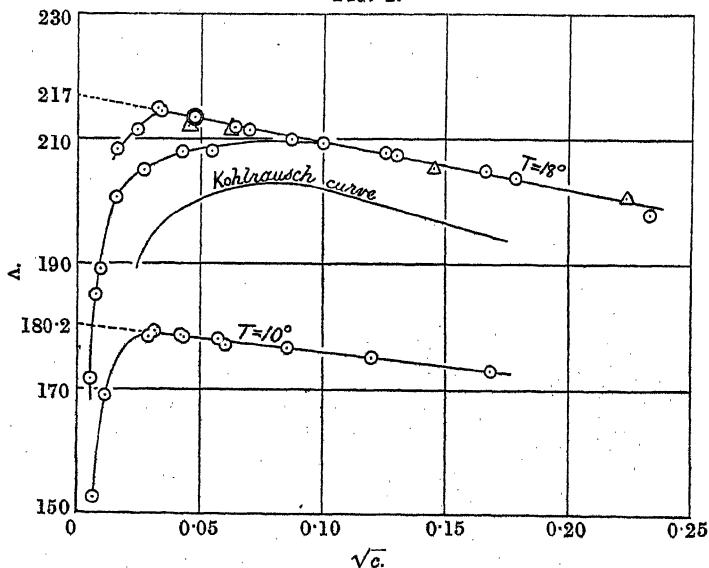
Noyes (*loc. cit.*), whose sodium hydroxide was estimated by himself to contain 0.1% of barium sulphate, gives four values for the equivalent conductivity which lie about 0.5% below our values (see Fig. 2).

For comparison, the values obtained by Kohlrausch (*Wied. Ann.*, 1885, 26, 197) are also plotted in Fig. 2.

*The Temperature Coefficient of Equivalent Conductivity between 10° and 18°.*—The temperature coefficient calculated from the above figures is 4.60. The value obtained by Noyes (*loc. cit.*) for the range 18–100° was also 4.60.

*The Mobility of the Hydroxyl Ion.*—The mobility of the sodium ion at 18° being taken as 43.4 (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, 34, 479), the mobility of the hydroxyl ion becomes 173.6 at 18°.

FIG. 2.



The points marked  $\Delta$  are those of Noyes; the concentrations have been recalculated to gram-mols. per litre.

If the mobility of the sodium ion as calculated by Washburn (*J. Amer. Chem. Soc.*, 1918, 40, 158) is taken to be 43.23, the value for the hydroxyl ion becomes 173.8.

On the somewhat untrustworthy assumption that the transport number of the hydroxyl ion in sodium hydroxide has the same value at 18° and 10°, the mobility of the hydroxyl ion at 10° is, using the Noyes and Falk value for the sodium ion, 144.2, and using the Washburn value, 144.3.

#### Summary.

The equivalent conductivity of solutions of sodium hydroxide has been measured at 18° and 10° and the values for infinite dilution found to be 217.0 and 180.2, respectively.

Using Washburn's value for the mobility of the sodium ion, the mobility of the hydroxyl ion is found to be 173.8 and 144.3 at the two temperatures.

The authors wish to express their indebtedness to the Research Fund Committee of the Chemical Society for assistance in purchasing a part of the apparatus used for the still, to the authorities of Balliol and Trinity Colleges for permission to use their laboratory, and in particular to Brigadier-General H. Hartley for his continued interest and advice during the course of the work.

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## LXXXVI.—*The Mercuration of Aromatic Substances.* *Part II. o-Nitrotoluene.*

By SAMUEL COFFEY.

THE position taken up by the acetoxymercuri-group in the mercuration of benzenoid compounds is sometimes anomalous; thus in the mercuration of nitrobenzene 50 and 40% of the *o*- and *m*-compounds respectively are formed, whilst with toluene the proportions of the three isomerides are  $o:m:p = 43:13:44$  (J., 1925, 127, 1029).

In the mercuration of the three mononitrotoluenes, which has now been studied, the reaction does not follow the expected course. This paper deals with the results obtained on mercuring *o*-nitrotoluene. When a third substituent is introduced into this compound, the 1:2:6 and 1:2:4-derivatives are generally the chief products. Of the four possible chloromercuri-*o*-nitrotoluenes, the 1:2:4-compound was isolated in quantity, the 1:2:6-compound was proved to be present in relatively large amounts, and the formation of the 1:2:3- or 1:2:5-derivative also was demonstrated. Attempts that were being made to discover which of these two was actually present were abandoned when the author was informed that Dr. Kenner, working at Sheffield, had obtained the 1:2:3-derivative in considerable quantity by mercuring *o*-nitrotoluene.

Although nitrotoluenes react with mercuric oxide and hot caustic soda solution to give compounds containing mercury in the side chain (Reissert, *Ber.*, 1907, 40, 4209), no mercurinitrotoluenes containing mercury directly attached to the nucleus are known. These are readily obtained when *o*-nitrotoluene is heated with mercuric acetate at 140°.

For comparison and in order to see whether the 1:2:3- and  
Y\*

1:2:5-derivatives differed at all in physical properties from the normal substitution products, 4-chloromercuri- and 5-chloromercuri-2-nitrotoluene were made synthetically through the corresponding sulphinic acids (compare Peters, *Ber.*, 1905, 38, 2567).

#### EXPERIMENTAL.

*Mercuration of o-Nitrotoluene.*—From the product of reaction in boiling acetic acid, only mercurous acetate and the internal anhydride of monohydroxymercuri-acetic acid were isolated.

The mercuration was best carried out as follows: Mercuric acetate (1 part) and *o*-nitrotoluene (4 parts) were heated gradually with occasional shaking. At 110–120°, the mercuric salt became orange-red and viscous, the solution frothed slightly, and acetic acid distilled off. As the temperature increased, the red mass gradually disappeared and a pale yellow solution formed. A temperature of 140–150° was attained after an hour's heating and was maintained until the product failed to respond to a test for mercuric ions (4 hours). After 12 hours, a brown, amorphous solid, containing a little free mercury but consisting mainly of mercurous acetate, separated.

The clear nitrotoluene solution was then poured into a large volume of ether and left for 24 hours, when an almost colourless, amorphous solid separated. This had a high mercury content and apparently consisted of polymercuri-compounds; it was free from monoacetoxymmercuri-derivatives. The ether was distilled off, the clear yellow solution treated with an excess of sodium chloride solution to convert the acetoxymmercuri-compounds into the more easily purified chloro-derivatives, and the excess of nitrotoluene removed as quickly as possible in a current of steam. The main product of the reaction remained as a heavy, almost colourless mass. This was broken up and allowed to dry in the air. The yields (in grams) of the various products obtained in different experiments were:

	I.	II.	III.	IV.
Nitrotoluene used .....	210	310	1000	360
Mercuric acetate .....	50	75	200	90
Insoluble in nitrotoluene .....	3	7½	18	5
Insoluble in ether .....	9	15½	35	15
Main product .....	40	55	166	69

This crude main product contained a small amount of nitrotoluene which was retained very tenaciously but was finally removed by extraction with ether in a Soxhlet apparatus. The residue melted at 120–155° and consisted only of monochloromercuri-*o*-nitrotoluenes (Found: N, 3.75.  $C_7H_6O_2NClHg$  requires N, 3.8%).

*Separation and Orientation of 4-Chloromercuri-2-nitrotoluene.*—By crystallising the crude product (160 g.) twice from 500 c.c. of hot

acetone the pure compound was obtained in silky needles, m. p. 220.5—221° (corr.), having, when dry, the appearance of asbestos. By working up the mother-liquors a total yield of 32 g. was obtained (Found: N, 3.7; Hg, 53.9. Calc., N, 3.8; Hg, 53.9%).

4-Chloromercuri-2-nitrotoluene is sparingly soluble in all usual solvents except acetone and hot glacial acetic acid. By treatment with the theoretical quantity of bromine in chloroform it was slowly but quantitatively converted into 4-bromo-2-nitrotoluene, which crystallised from methyl alcohol in slender needles, m. p. 44.5—45°; when it was crystallised very slowly it was obtained in large, pale yellow, brittle prisms (compare Hübner and Roos, *Ber.*, 1873, 6, 799).

Most organic mercury compounds react with iodine very readily, but the reaction of 4-chloromercuri-2-nitrotoluene with an equivalent of iodine in chloroform required 11 or 12 days for completion, theoretical yields being obtained of mercuric chloride, mercuric iodide, and 4-iodo-2-nitrotoluene, which crystallised from methyl alcohol in small, brittle prisms, m. p. 60.5—61°, identical with that obtained by Heynemann (*Annalen*, 1871, 158, 345) and Reverdin (*Ber.*, 1897, 30, 3001).

4-Bromomercuri-2-nitrotoluene was prepared by treating a solution of the chloro-compound in aqueous acetone with potassium bromide; after boiling for a few minutes, it was cooled, filtered, and the solid washed with water, and recrystallised from acetone. It is a heavy, crystalline powder, m. p. 241° (corr.), less soluble than the chloro-compound.

4-Iodomercuri-2-nitrotoluene, prepared in a similar manner, melts at 286° with slight decomposition. It was recrystallised from acetone, in which it was only sparingly soluble.

4-Mercuribis-2-nitrotoluene.—No mercuri-bis-nitro-compounds are known with the exception of mercuribistrinitrobenzene, obtained by heating mercuric trinitrobenzoate. The mercuribisnitrotoluene was obtained by carefully reducing the above chloro-compound with the calculated quantity of sodium sulphide. Under these conditions the chloromercuri-group is attacked before the nitro-group, owing no doubt to the fact that *o*-nitrotolyl mercuric sulphide is first formed and this unstable compound on warming undergoes spontaneous decomposition. In this way, the reducing agent is effectually "fixed" and cannot react with the nitro-group.

4-Chloromercuri-2-nitrotoluene (3.7 g.) was shaken in a solution of crystallised sodium sulphide (1.2 g.) for 3 hours, being thereby converted into the colourless sulphide. The mixture was heated on the water-bath for 2 hours, the black product filtered off, washed, dried, boiled with acetone, and the solution filtered hot. The black,

inky extract, containing colloidal mercuric sulphide, thus obtained was filtered again when cold, the black, colloidal mercuric sulphide passing through the filter and leaving a white, crystalline solid. This spectacular method of purification was repeated until no more solid was obtained. The product was pure 4-mercuribis-2-nitrotoluene, which crystallises from acetone in a woolly mass of needles, m. p.  $291^{\circ}$  (corr.) (Found: Hg, 42.0.  $C_{14}H_{12}O_4N_2Hg$  requires Hg, 42.4%). On boiling for 3 hours with one equivalent of mercuric chloride in alcohol, it gave an almost theoretical yield of pure 4-chloromercuri-2-nitrotoluene, its constitution being thus determined.

*Existence of 6-Chloromercuri-2-nitrotoluene.*—The remainder of the mixed chloromercurinitrotoluenes (see p. 638) was suspended in chloroform and treated with bromine (1 mol.), and the bromonitrotoluenes, which were purified by distillation in steam, were obtained in quantitative yield as a golden-yellow oil, freezing at low temperatures to a buttery mass. Attempts to separate this oil into its constituents by means of freezing, fractional distillation in steam, or a vacuum, or by crystallisation, failed. The nitro-compounds were therefore reduced to the corresponding bromotoluidines by warming for 2 hours with sodium sulphide in aqueous alcoholic solution on the water-bath. The amines were distilled in steam, an excess of hydrochloric acid was added to the distillate, and the mixed hydrochlorides were fractionally crystallised; but no pure compound could thus be isolated. The mixture of bases was therefore acetylated, and 7.2 g. of the product were fractionally crystallised as follows. The solution in 50 c.c. of hot 50% acetic acid was filtered, and cooled very rapidly, when 2.1 g. (A) separated, m. p.  $150-158^{\circ}$ . On standing, the mother-liquor deposited 0.7 g. (B) of pale brown needles, m. p.  $159-161^{\circ}$ . Only solids with low melting points could be obtained from the final mother-liquor.

On recrystallisation from 10 c.c. of 50% acetic acid (A) gave 1.6 g., m. p.  $163-164^{\circ}$ , and further recrystallisation from benzene furnished colourless needles of constant m. p.  $165.5^{\circ}$  (corr.). On hydrolysis this acetyl compound gave a base, m. p.  $32^{\circ}$ , which was converted into a benzoyl derivative, m. p.  $160^{\circ}$  (corr.). The base was compared with 4-bromo-*o*-toluidine; the latter also melted at  $32^{\circ}$ , and its acetyl derivative at  $165.5-166^{\circ}$  (compare Janney, *Annalen*, 1913, 398, 359), as did also a mixture with (A). The benzoyl compounds were also identical. The yield of 4-bromoaceto-*o*-toluidide isolated was 23%, corresponding to 18% of the original mixed mercurated nitrotoluenes. Hence the total amount of 4-chloromercuri-2-nitrotoluene accounted for is 38%.

The product (B) on recrystallisation from benzene gave 0.55 g.

of long needles, m. p. 162—163°; a mixture with (A) melted at 120—130°. Hydrolysis furnished a liquid base, which was proved to be 6-bromo-*o*-toluidine as follows: 2:6-dinitrotoluene was reduced, as described by Noeltig (*Ber.*, 1904, **37**, 1018), to 6-nitro-*o*-toluidine. This was diazotised and converted into 6-bromo-*o*-nitrotoluene, m. p. 38°. The latter was reduced to a liquid base, which gave a theoretical yield of the acetyl compound (B) on treatment with acetic anhydride; it melted at 164.5° (corr.).

Some of the melting points of this acetyl compound given in the literature are erroneous; Friedländer, Bruckner, and Deutsch (*Annalen*, 1912, **388**, 30) give it as 163°.

*Proof of the Presence of 3- or 5-Chloromercuri-2-nitrotoluene.*—Many attempts were made to isolate other derivatives of the bromotoluidines, the bromodinitrotoluenes (obtained by nitrating the mixture of bromonitrotoluenes), or the nitrotoluenesulphonic acids (obtained by sulphonating the original mercuri-compounds), but without success. A small quantity of 3:5-dibromo-*o*-toluidine was isolated, which indicated the presence of one or both of the compounds in question, but a more direct proof was obtained by eliminating the amino-group from the mixed bromotoluidines and showing the presence of *m*-bromotoluene in the product.

A mixture of the dry amines, absolute alcohol (4 parts), and 20% oleum (2 parts) was warmed with an excess of sodium nitrite, and the product distilled in steam. The bromotoluenes, which passed over together with a brown substance, were purified by steam distillation from an alkaline solution and repeated fractional distillation, a colourless liquid, b. p. 179—190°, being finally obtained which only partly solidified at —80°. Hence it was not a mixture of the *o*- and *p*-isomerides only. The mixture was oxidised to the corresponding bromobenzoic acids, and the latter were separated as already described in Part I. In this way pure *m*-bromobenzoic acid, m. p. 154°, was isolated, the presence thus being proved of a substance in the original mixture having the chloromercuri-group in the meta-position with respect to a methyl group and in the ortho- or para-position with respect to a nitro-group; which is abnormal for direct substitution.

*Synthesis of 5-Chloromercuri-2-nitrotoluene. Preparation of 2-Nitrotolyl 2-Nitrotoluene-5-sulphazide.*—Almost all the nitrotoluene-sulphinic acids are unknown. Since the usual methods of preparation failed here, a process devised by Limpricht (*Ber.*, 1887, **20**, 1238) was used.

Sulphur dioxide was passed into a suspension of 6-nitro-*m*-toluidine (10 g.) in 100 c.c. of alcohol at 0° until absorption ceased. The resulting solution was treated at 0° with nitrous fumes or with

a saturated solution of 20 g. of potassium nitrite with constant stirring. The mixture was kept in ice over-night and at room temperature for 2 days and then poured into water. The bright orange precipitate (9 g.) thus obtained was extracted with boiling alcohol, in which it was only sparingly soluble, and crystallised from glacial acetic acid, 2-nitrotolyl 2-nitrotoluene-5-sulphazide separating in deep orange prisms, m. p. 157—158° (violent decomp.) (Found: N, 15.5.  $C_{14}H_{14}O_6N_4S$  requires N, 15.3%).

Fission of a sulphazide by boiling sodium hydroxide solution usually proceeds smoothly:  $R \cdot SO_2 \cdot NH \cdot NHR' + NaOH = R \cdot SO_2Na + R'H + N_2 + H_2O$  (compare Escales, *Ber.*, 1885, 18, 896). From the nitrotoluene compounds, however, much tar was produced and the acids were difficult to obtain pure by the usual methods. In the preparation of 2-nitrotoluene-5-sulphinic acid and other nitrosulphinic acids good use has been made of the fact that they form insoluble ferric salts, which are unchanged by dilute acids (Thomas, J., 1909, 95, 342).

The preceding sulphazide was boiled with a slight excess of baryta until no more nitrotoluene escaped with the steam. The deep reddish-brown solution was filtered hot through a wet filter to remove tar, acidified, well diluted, filtered from a little more tar, and treated with an excess of ferric chloride solution. The copious precipitate of ferric salt obtained was boiled with ammonia, the solution filtered from ferric oxide and evaporated to a small volume. On acidification a pale yellow oil separated. This was extracted with ether, and on removal of the solvent, 2-nitrotoluene-5-sulphinic acid separated in small, colourless needles (Found: equiv., 203.  $C_7H_7O_4NS$  requires equiv., 201.1. Found for the ferric salt: Fe, 8.3.  $C_{21}H_{18}O_{12}N_3S_3Fe$  requires Fe, 8.3%).

The sulphinic acid was boiled with a 50% aqueous alcoholic solution of mercuric chloride for a week, the solid which separated being filtered off periodically. After washing and drying, the crude chloromercuri-compound was extracted with hot acetone; pure 5-chloromercuri-2-nitrotoluene crystallised from the solution in a felted mass of small, shining needles, m. p. 210°. In solubility and general properties it was very similar to the 4-isomeride.

*2-Nitrotoluene-4-sulphinic Acid.*—When a dilute solution of diazotised 6-nitro-*p*-toluidine was treated with sulphur dioxide and copper powder, a tarry mass was produced immediately. Better results were obtained by working in strongly acid solution, but even then the sulphazide was produced and not the free acid. The base (10 g.) was dissolved in sulphuric acid (75 c.c.) and water (75 c.c.), cooled to 0°, and diazotised; the latter reaction took place very slowly. The solution was saturated at 0° with sulphur

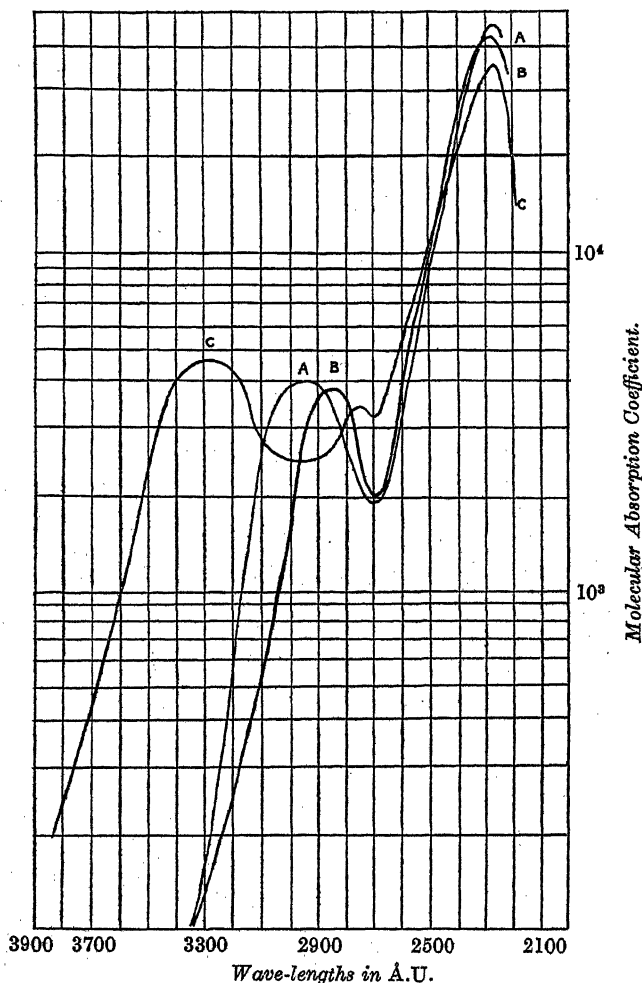




physiological effect, and further absorption spectrum study was undertaken to investigate this important phase of the subject.

Acetylthyroxin was prepared by Kendall's method (*loc. cit.*) from 20 mg. of commercial thyroxin. It remained amorphous and gummy,

FIG. 1.



A, keto-Thyroxin. B, Acetylthyroxin. C, Thyroxin in alkaline solution.

despite attempts to purify it by crystallisation from alcohol. Through the courtesy of Dr. Kendall, who specially prepared a specimen of the acetyl derivative from pure thyroxin, measurements of the absorption were made possible. The substance was dissolved

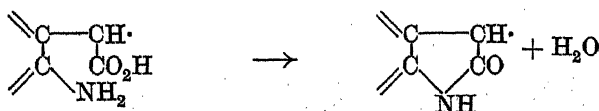
in 75% aqueous alcohol and examined in concentrations of  $M/2,000$ ,  $M/8,000$ ,  $M/20,000$ ,  $M/50,000$ , and  $M/100,000$ .

*keto*-Thyroxin was prepared by dissolving the pure substance in 75% alcohol containing four equivalents of hydrochloric acid, and measurements were made at the same concentrations as the above.

The alcohol-soluble derivative obtained by passing carbon dioxide into a solution containing thyroxin and its equivalent of sodium hydroxide (*loc. cit.*) was dissolved in the minimum of 60% alcohol, and measurements were made as rapidly as possible at concentrations of  $M/4,000$ ,  $M/20,000$ ,  $M/80,000$ , and  $M/100,000$ .

### Discussion.

Allowance must be made for the error in the value of the absorption coefficient likely to arise from the use of such minute quantities of material, but even so the evidence of the wave-lengths of the absorption bands remains. The curves for the acetyl derivative and the *keto*-form of thyroxin are more closely related to each other than to the curve for thyroxin in alkaline solution. The major band in the last lies at 3275 Å.U., whilst in the other two it lies respectively at 2850 Å.U. and 2925 Å.U., the third band at 2750 Å.U. being absent from both. The curve for the so-called open-ring form, prepared by the action of carbon dioxide on an alkaline solution of thyroxin, is almost identical with that for the *keto*-form, except that it tails off suddenly at 2400 Å.U., in the region of  $\log \epsilon = 4$ , into the Schumann region, giving no band as in the other cases. It is possible that during the time taken to make the measurements, even in dilute alcohol, water may be removed, with consequent closure of the ring, and therefore the results obtained may be intermediate values. The change is represented as follows :



Since the original measurements were made on thyroxin, Friedli has confirmed the presence of the band in indole, in the region 2100 Å.U. (*Bull. Soc. chim. Biol.*, 1924, 6, 10, 908).

My thanks are due to Professor Sir F. Gowland Hopkins for his continued interest in the work, and to Dr. E. C. Kendall for the gift of acetylthyroxin. This work was done during the tenure of a Beit Memorial Fellowship for Medical Research.

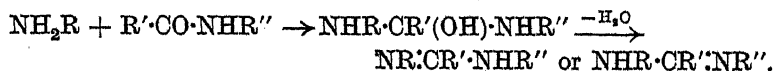
LXXXVIII.—*N*-Alkylated Amidines.

By MONMOHAN SEN and JÑANENDRA NATH RÂY.

IN connexion with certain investigations relating to glyoxaline alkaloids, it became necessary to prepare and study the behaviour of a number of *N*-alkylated amidines. The methods already available for the preparation of these substances (Wallach, *Ber.*, 1879, 12, 328; 1882, 15, 208; 1883, 16, 357, 1647; Strecker, *Annalen*, 1857, 103, 328) are not entirely satisfactory. Hofmann (*Jahresber. Fort. Chem.*, 1865, 414; *Monatsberichte Berl. Akad.*, 1865, 640) obtained diphenylacetamidine and diphenylbenzamidine by condensing aniline with acetanilide and benzanilide, respectively, in presence of phosphorus trichloride or pentachloride. This rather convenient method seems to have been little investigated and it was deemed desirable to study it systematically. It is of very general applicability and by its means a number of new amidines have been prepared, in good yield in most cases. Phosphorus trichloride is the most suitable condensing agent for the purpose, although phosphoric oxide in boiling xylene may advantageously replace it in some cases.

A mixture of the requisite quantities of an amine and an acylamine in about ten times the weight of phosphorus trichloride is heated at 110–120° for about 3 hours. The completion of the reaction is indicated by a drop of the reaction mixture giving a clear solution in water. The product is dissolved in cold water and basified; the amidine is then precipitated in a crystalline condition.

The method is applicable to a secondary amine like diphenylamine and an acylamine. On the other hand, acetomethylanilide condenses with *m*-toluidine, hence the reaction is represented as taking place as follows :

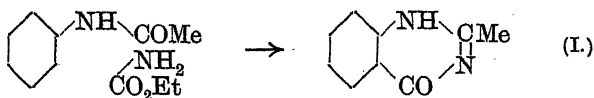


But no isomeric forms can be isolated, as the amidines show virtual tautomerism (compare von Pechmann, *Ber.*, 1895, 28, 869). By altering the order of combination the same product was isolated (A) from acetanilide and *m*-toluidine and from aceto-*m*-toluidine and aniline, and (B) from acetanilide and *p*-nitroaniline and from *p*-nitroacetanilide and aniline. The result (B) is interesting, as here a strongly negative group in the molecule has not impaired the mobility of the hydrogen atom in any way.

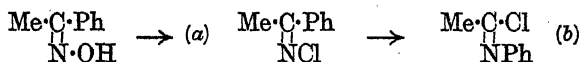
With a view to prepare hydrazidines, we attempted to condense an acylamine with phenylhydrazine by this method. The product

of interaction of acetanilide and phenylhydrazine, on being rendered alkaline, evolved ammonia and diphenylacetamidine was obtained in more than 70% yield.

Next, we attempted to prepare cyclic amidines by using urethane in place of an amine. Phosphoric oxide acting on molar proportions of acetanilide and urethane in boiling xylene solution gave rise to the compound (I), which will be described along with others of the same series in a subsequent communication.



A further point of interest is in connexion with the Beckmann transformation of acetophenoneoxime. The transformation may be represented as taking place through the phases (a) and (b):



Both (a) and (b) represent reactive chloro-compounds capable of condensing with aniline to form acetophenonephenylhydrazone and diphenylacetamidine respectively. The actual amounts of each would depend on the relative reactivity of the two chlorine atoms in (a) and (b). Actually, the amidine was produced and no trace of acetophenonephenylhydrazone could be detected. This result may, of course, be due to the smaller reactivity of the chlorine atom in the group C:NCl as compared with N:Cl, but it may also be taken to indicate that the intermediate phase (a) exists only for a very short period of time.

#### EXPERIMENTAL.

Some properties of the amidines that have been prepared are tabulated below. Unless stated otherwise, the amidines were crystallised from alcohol. The values in brackets in column 3 are the calculated percentages of nitrogen. An amidine X:NY was prepared from the components XO and NH<sub>2</sub>Y; e.g.,

NHPh·CMe:N·C<sub>6</sub>H<sub>4</sub>Me  
from NHPh·COMe and C<sub>6</sub>H<sub>4</sub>Me·NH<sub>2</sub>, and so on.

Formula.	M. p.	N %.	Remarks.
NHPh·CMe:N·C <sub>6</sub> H <sub>4</sub> Me (m).	103°	*12.7 (12.5)	Needles.
" (p).	90	12.7	"
" (o).	138	12.9	Buff-coloured needles.
NHPh·CMe:N·C <sub>6</sub> H <sub>4</sub> ·NO <sub>2</sub> (p).	189	16.9 (16.5)	Yellow, prismatic needles.†
NHPh·CMe:N·C <sub>6</sub> H <sub>4</sub> ·OEt (p).	102	11.3 (11.0)	Colourless needles.

\* C, 80.2 (80.3); H, 7.3 (7.1).

† From methyl alcohol.

Formula.	M. p.	N %.	Remarks.
$\text{NPh}\cdot\text{CMe}\cdot\text{NPh}_2$ .	92	10.1 (9.8)	Prismatic needles.
( <i>m</i> ) $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CMe}\cdot\text{NPh}$ .	103	12.8 (12.5)	Identical with the first.
( <i>m</i> ) $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}(\text{o})$ .	101	12.1 (11.8)	Rectangular plates.
( <i>p</i> ) " " " " ( <i>p</i> ).	120	11.5	Needles.*
( <i>p</i> ) $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(\text{m})$ .	134	15.9 (15.6)	Product boiled with water before crystallisation. Yellow needles.*
( <i>p</i> ) $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CMe}\cdot\text{NPh}_2$ .	122	9.4 (9.3)	Needles.
( <i>p</i> ) $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt}(\text{p})$ .	117	9.6 (9.6)	"
$\text{NPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}(\text{o})$ .	107	10.0 (9.8)	"
( <i>p</i> ) $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}(\text{o})$ .	122	9.4 (9.2)	Elongated needles.
$\text{NPhMe}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}(\text{m})$ . (picrate)	157	15.2 (15.0)	The base is an oil. Isolated as the picrate. Bright yellow needles. The free base regenerated from the picrate is an oil which could not be solidified.
( <i>p</i> ) $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CMe}\cdot\text{NPh}$ .	189	—	Mixed with the fourth compound, no lowering of m. p. observed.
$\text{NPh}\cdot\text{CMe}\cdot\text{NPh}$ .	—	—	From acetanilide and phenylhydrazine.

\* From dilute alcohol.

We wish to thank Professor R. Robinson, F.R.S., for his kind help in the preparation of the manuscript.

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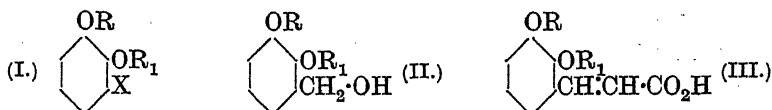
[Received, November 28th, 1925.]

## LXXXIX.—Substitution in Vicinal Trisubstituted Benzene Derivatives. Part IV.

By LEON RUBENSTEIN.

THE investigation of substitution in dialkylxybenzene derivatives of type (I) in which the group X is meta-directing has been conducted on a large number of compounds and discussed at length (Davies and Rubenstein, J., 1923, 123, 2839; Rubenstein, J., 1925, 127, 2268).\* The continuation of that work is now described.

\* The bromination of these dialkylxyaldehydes has been stated (*loc. cit.*) to give only the 5-bromo-derivative, the argument being based upon (i) the position of substitution of the salicylaldehyde derivatives and (ii) the capacity of the brominated product to give a 6-nitro-compound. The position of the bromine atom in these compounds has now been proved by the direct preparation of 5-bromo-*o*-veratric acid from 5-nitro-*o*-veratric acid (see p. 652).



Substitution processes have been investigated on vicinal substances of type (I) in which X is a weakly ortho-para-orienting group. The first series of compounds examined as fulfilling these requirements were the dialkyloxybenzyl alcohols, and the nitration and bromination of these substances were carried out. In the nitration of *o*-veratryl alcohol, 2:3-diethoxybenzyl alcohol, and 3-methoxy-2-ethoxybenzyl alcohol good yields of the 5-nitro-benzyl alcohol were obtained in each case, the position of the nitro-group being shown by oxidation of the benzyl alcohol derivative to the corresponding benzoic acid. Bromination did not proceed so smoothly, but moderate yields of the 5-bromo-benzyl alcohols were obtained, the place of substitution again being shown by oxidation. The second series of compounds examined were the dialkyloxy-cinnamic acids (III) in which the group X (I) is ortho-para-orienting and unsaturated. In this case again, 5-nitro-derivatives were produced exclusively in the case of 2:3-diethoxycinnamic and 3-methoxy-2-ethoxycinnamic acids. From these substances, the respective benzoic acids were reformed on oxidation. From 2:3-dimethoxycinnamic acid a mixture of isomerides was formed on nitration, and by fractionally separating first the acids and then the esters left in the residual mixture on esterification it was shown that 85% of the nitration mixture consisted of 5-nitro-2:3-dimethoxycinnamic acid, the rest being the 6-nitro-acid.

#### EXPERIMENTAL.

**5-Nitro-2:3-dimethoxybenzyl Alcohol.**—2:3-Dimethoxybenzyl alcohol (5.5 g.; prepared from *o*-veratraldehyde by means of the Cannizzaro reaction) dissolved in glacial acetic acid (20 c.c.) is treated gradually with a solution of nitric acid (5.5 c.c., *d* 1.42) in glacial acetic acid (5.5 c.c.); the temperature rises to 40–50°. After being maintained at 50° for 2 hours and at room temperature over-night, the brown solution is poured into water. The product, an oil which slowly solidifies, crystallises from methyl alcohol in colourless needles, m. p. 67° (yield 90%) (Found: N, 6.6.  $\text{C}_9\text{H}_{11}\text{O}_5\text{N}$  requires N, 6.6%). On oxidation with alkaline permanganate solution and subsequent acidification with dilute hydrochloric acid 5-nitro-*o*-veratric acid is obtained, m. p. 176°, identical with the acid obtained by the nitration of *o*-veratric acid.

**3-Methoxy-2-ethoxybenzyl Alcohol.**—3-Methoxy-2-ethoxybenzaldehyde (12 g.) dissolved in methyl alcohol (16 c.c.) is treated with

a solution of potassium hydroxide (17.6 g.) in methyl alcohol (45 c.c.). After 24 hours, the greater portion of the methyl alcohol is distilled off, the residue shaken with benzene, the extract washed a few times with concentrated sodium bisulphite solution and dried over potassium carbonate, and the benzene evaporated. The residual oil almost wholly distills at reduced pressure as a colourless liquid, b. p.  $148^{\circ}/13$  mm. (yield, almost theoretical).

*5-Nitro-3-methoxy-2-ethoxybenzyl Alcohol.*—3-Methoxy-2-ethoxybenzyl alcohol (2 g.) dissolved in glacial acetic acid (2 c.c.) is treated with a solution of nitric acid (2 c.c.) in glacial acetic acid (2 c.c.), and the reddish-brown solution kept over-night. The 5-nitro-3-methoxy-2-ethoxybenzyl alcohol which separates in pale yellow, prismatic crystals is filtered off; more is obtained on pouring the filtrate into water and crystallising the oily product, which hardens, from alcohol; m. p.  $132^{\circ}$  (yield 65%) (Found: N, 6.4.  $C_{10}H_{13}O_5N$  requires N, 6.2%). On oxidation with an alkaline solution of potassium permanganate 5-nitro-3-methoxy-2-ethoxybenzoic acid, m. p.  $169^{\circ}$ , is obtained.

*2:3-Diethoxybenzyl Alcohol.*—This is obtained from 2:3-diethoxybenzaldehyde and purified substantially by the process described under 3-methoxy-2-ethoxybenzyl alcohol. It is a colourless oil, b. p.  $163^{\circ}/11$  mm.,  $167^{\circ}/19$  mm., which solidifies on cooling and can be crystallised from light petroleum (b. p.  $60-80^{\circ}$ ), separating in colourless needles, m. p.  $35^{\circ}$  (Found: C, 67.6; H, 8.0.  $C_{11}H_{16}O_3$  requires C, 67.4; H, 8.2%).

*5-Nitro-2:3-diethoxybenzyl Alcohol.*—This is obtained from 2:3-diethoxybenzyl alcohol (1.5 g. in glacial acetic acid, 2 c.c.) and nitric acid (1.5 c.c. in glacial acetic acid, 1.5 c.c.) by the method described under 5-nitro-2:3-dimethoxybenzyl alcohol. It crystallises from alcohol in colourless needles, m. p.  $75^{\circ}$  (yield 1.7 g. or 90%) (Found: N, 7.2.  $C_{11}H_{15}O_5N$  requires N, 7.1%), and on oxidation with 1% alkaline permanganate yields 5-nitro-2:3-diethoxybenzoic acid, m. p.  $118^{\circ}$ , identical with the nitration product of 2:3-diethoxybenzoic acid.

*5-Bromo-2:3-dimethoxybenzyl Alcohol.*—*o*-Veratryl alcohol (5 g.), dissolved in glacial acetic acid (25 c.c.) containing sodium acetate (7.5 g.), is treated with bromine (5 g.) in glacial acetic acid (20 c.c.). After 2 days, the mixture is poured into water. The oil that separates, and hardens slowly, is removed (3.5 g.), and the filtrate treated with solid sodium bicarbonate; a further 3.7 g. of solid are then obtained. The combined products, crystallised from light petroleum a few times, yield 5-bromo-2:3-dimethoxybenzyl alcohol in colourless needles, m. p.  $82^{\circ}$  (Found: Br, 31.8.  $C_9H_{11}O_3Br$  requires Br, 32.1%). The acid produced by its oxidation with



1% alkaline potassium permanganate at 60—70°, after crystallisation from light petroleum, melts at 120° and does not depress the m. p. of 5-bromo-*o*-veratric acid obtained by oxidation of 5-bromo-*o*-veratraldehyde.

*5-Bromo-3-methoxy-2-ethoxybenzyl Alcohol*.—3-Methoxy-2-ethoxybenzyl alcohol (2 g.) is brominated by the foregoing method. The oil produced on dilution, after hardening, is isolated by means of benzene and crystallised twice from light petroleum (b. p. 60—80°); 5-bromo-3-methoxy-2-ethoxybenzyl alcohol is thus obtained in white prisms, m. p. 55—56° (Found: Br, 30.3.  $C_{10}H_{13}O_3Br$  requires Br, 30.6%).

*5-Bromo-2 : 3-diethoxybenzyl Alcohol*.—2 : 3-Diethoxybenzyl alcohol (2.5 g.) dissolved in glacial acetic acid (13 c.c.) containing sodium acetate (4 g.) is treated at 20—25° with bromine (2 g.) in glacial acetic acid (7 c.c.). After remaining in sunlight for a few days, the mixture is poured into water; the oil obtained partly solidifies after several days. The oily portion is removed as completely as possible, and the residue crystallised three times from light petroleum; 5-bromo-2 : 3-diethoxybenzyl alcohol is thus obtained in colourless, prismatic crystals, m. p. 60° (Found: Br, 28.6.  $C_{11}H_{15}O_3Br$  requires Br, 29.1%).

*Nitration of 2 : 3-Dimethoxycinnamic Acid*.—The finely powdered acid (5 g.) is added in small portions and with stirring to nitric acid (25 c.c.; *d* 1.42). After 3 hours, the mixture is poured over ice. The cream-coloured precipitate (6 g.) is dried and dissolved in boiling alcohol. By careful fractional separation 3.3 g. of a substance, m. p. 205—227°, are obtained. The alcoholic filtrate is evaporated to small bulk, saturated with hydrogen chloride, and heated on a water-bath for 1 hour. Fractional separation of the mixture of esters thus produced yields first *ethyl 5-nitro-2 : 3-dimethoxycinnamate*, which crystallises from alcohol in cream, prismatic needles, m. p. 111° (Found: N, 5.2.  $C_{13}H_{15}O_6N$  requires N, 5.0%). [*5-Nitro-2 : 3-dimethoxycinnamic acid* is obtained, by twice crystallising the product, m. p. 205—227°, in pale yellow prisms, m. p. 229° (Found: equiv., 256.  $C_{11}H_{11}O_6N$  requires equiv., 253). Oxidation with potassium permanganate gives 5-nitro-*o*-veratric acid.] *Ethyl 6-nitro-2 : 3-dimethoxycinnamate* is obtained from later fractions and crystallises from aqueous alcohol in long, white needles, m. p. 86°. It is hydrolysed by boiling for a few minutes with equal volumes of water, glacial acetic acid, and sulphuric acid, giving 6-nitro-2 : 3-dimethoxycinnamic acid, which crystallises from aqueous alcohol in brown needles, m. p. 210—215° (decomp.). On oxidation with alkaline potassium permanganate solution at 90° and acidification, it gives a substance of high m. p.

(above 280°) which appears to be identical with the 6-nitro-3-hydroxy-2-methoxybenzoic acid obtained by boiling 6-nitro-2:3-dimethoxybenzoic acid for 15 hours with 2.5 *N*-sodium hydroxide.

**3-Methoxy-2-ethoxycinnamic Acid.**—3-Methoxy-2-ethoxybenzaldehyde (6 g.) is added to pyridine (20 c.c.) containing malonic acid (7.2 g.), 6 drops of piperidine are added, and the solution is heated under reflux on a steam-bath for 1 hour; the evolution of carbon dioxide is then completed by boiling the solution for 5 minutes. The cooled solution is poured into water acidified with concentrated hydrochloric acid, and the precipitate of 3-methoxy-2-ethoxycinnamic acid (yield almost quantitative) collected. It crystallises from alcohol in colourless needles, m. p. 151° (Found: equiv., 220.  $C_{12}H_{14}O_4$  requires equiv., 222).

**5-Nitro-3-methoxy-2-ethoxycinnamic Acid.**—Finely divided 3-methoxy-2-ethoxycinnamic acid (1 g.) is added gradually to nitric acid (10 c.c.; *d* 1.42), and the mixture kept over-night. On dilution with water 5-nitro-3-methoxy-2-ethoxycinnamic acid is obtained in quantitative yield. Crystallised from alcohol, it gives cream needles, m. p. 200–201° (Found: equiv., 269.  $C_{12}H_{13}O_6N$  requires equiv., 267).

**2:3-Diethoxycinnamic Acid.**—This acid, prepared from 2:3-diethoxybenzaldehyde (5 g.) by the pyridine method described above (yield 5.3 g. or 90%), crystallises from alcohol in long, slender, colourless needles, m. p. 161° (Found: equiv., 235.  $C_{13}H_{16}O_4$  requires equiv., 236).

**5-Nitro-2:3-diethoxycinnamic Acid.**—Prepared (at 20–25°) from 2:3-diethoxycinnamic acid (1 g.) and isolated by the method described under 5-nitro-3-methoxy-2-ethoxycinnamic acid, this acid is obtained in quantitative yield. It crystallises in long, cream prisms, m. p. 199° (Found: equiv., 280.5.  $C_{13}H_{15}O_6N$  requires equiv., 281).

The following is an account of the preparation of 5-bromo-*o*-veratric acid from 5-nitro-*o*-veratric acid.

5-Nitro-2:3-dimethoxybenzoic acid (4.5 g.) is heated with concentrated hydrochloric acid (15 c.c.) and tin (4.5 g.) on a steam-bath for a few hours, the solution diluted with water, the tin removed as sulphide, and the colourless filtrate evaporated under reduced pressure; white, prismatic crystals of the hydrochloride of 5-amino-2:3-dimethoxybenzoic acid are deposited (yield 80%).

The hydrochloride is soluble in water or alcohol and in warm concentrated hydrochloric acid, from which it can be crystallised. The solutions turn pink and then red in the air, especially if in presence of an excess of acid. 5-Amino-2:3-dimethoxybenzoic acid is obtained by treating a concentrated solution of the hydrochloride

with solid sodium carbonate until it is just acid to Congo-red. The colourless needles, m. p.  $250^{\circ}$  (decomp.), soon become deep-red owing to oxidation, and are soluble in acids and in alkalis (Found : N, 6.9.  $C_9H_{12}O_4N$  requires N, 7.0%).

The hydrochloride (4 g.) is dissolved in water (17 c.c.), neutralised with solid sodium carbonate, treated with hydrobromic acid (7.5 c.c.;  $d$  1.50), and diazotised at  $0^{\circ}$  with sodium nitrite (1.2 g. in water, 3 c.c.). The black, semi-crystalline solid obtained by heating the diazonium solution with cuprous bromide and concentrated hydrobromic acid is boiled with alcohol and animal charcoal, and the hot filtered solution cooled after addition of a little water. Long, cream needles are deposited, m. p.  $112-113^{\circ}$ , which, after further treatment with animal charcoal and recrystallisation from aqueous alcohol, melt at  $120^{\circ}$  and do not depress the m. p. of 5-bromo-*o*-veratric acid obtained by oxidation of 5-bromo-*o*-veratraldehyde.

The author is indebted to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this investigation.

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### XC.—*The Decomposition of Substituted Carbamyl Chlorides by Hydroxy-compounds. Part II. The Influence of the Hydroxy-compound.*

By TUDOR WILLIAMS PRICE.

IN Part I (J., 1924, 125, 115) an account was given of the reaction between phenylmethylcarbamyl chloride and ethyl alcohol at different temperatures. An account is now given of the reaction between phenylmethylcarbamyl chloride and various hydroxy-compounds at  $100^{\circ}$ .

Norris and Ashdown (*J. Amer. Chem. Soc.*, 1925, 47, 837) studied the reaction between various alcohols and *p*-nitrobenzoyl chloride in ether at  $25^{\circ}$ , but no quantitative work, so far as the author is aware, has hitherto been published on the influence of the constitution of the hydroxy-compound upon the velocity of reaction with a carbamyl chloride.

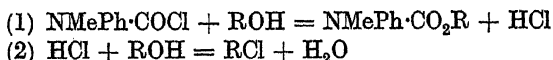
*Materials.*—The phenylmethylcarbamyl chloride was from the same batch as was used in the previous work, and had been kept over phosphoric oxide in a desiccator.

The various alcohols used were the purest commercial alcohols

and were all treated twice at their respective boiling points with fresh calcium turnings (1.0 and 0.5% by weight) and fractionated. The other hydroxy-compounds, which also were the purest commercial substances, were purified by fractional distillation, some under reduced pressure. Each hydroxy-compound after purification boiled either constantly at one temperature or over a range of less than  $0.2^{\circ}$ .

*Method of Work.*—In each experiment, 0.424 g. of the carbamyl chloride (equivalent to 25 c.c. of *N*/10-solution) and 5 c.c. of the hydroxy-compound were sealed in a test-tube and heated at  $100^{\circ}$  for a definite time. A hydroxy-compound that was solid at the ordinary temperature was first melted and 5 c.c. were placed in the tube, which was then cooled before the carbamyl chloride was introduced. These proportions caused the hydroxy-compound to be present in large excess, thus making the reaction unimolecular with respect to the carbamyl chloride.

In the case of the alcohols the whole reaction is made up of two consecutive reactions:



but the progress of the first reaction can be studied by determining the amount of carbamyl chloride left in the system at any instant. This was done, for those alcohols (methyl, ethyl, and *n*-propyl) which give low-boiling chlorides, in the manner described in Part I (*loc. cit.*). For the other hydroxy-compounds, since aspiration of air through the system would not remove the chloro-compound formed, the following method was used. After being heated at  $100^{\circ}$  for the required time, the mixture was titrated with *N*/10-potassium hydroxide. Excess of ammonia was then added to convert any unchanged carbamyl chloride into ammonium chloride and the corresponding substituted carbamide. The solution, after standing in the cold for 1 hour to complete the conversion, was extracted four times with light petroleum to remove the chloro-derivative of the hydroxy-compound, acidified with pure nitric acid, and titrated with *N*/10-silver nitrate without an indicator. This titre was a measure of both the ammonium chloride and the hydrogen chloride present. The amount of the latter was known from the *N*/10-potassium hydroxide titre, and by subtraction the ammonium chloride titre, which was equivalent to the carbamyl chloride, was obtained.

In the case of *n*-propyl alcohol both methods were employed, and gave almost identical results.

The quantity of phenylmethylcarbamyl chloride present being

known, the velocity coefficient for a unimolecular reaction was calculated from the expression

$$k = \frac{1}{t_2 - t_1} \log_e \frac{a - x_1}{a - x_2},$$

where  $t_1$  is 5 minutes and  $a - x_1$  is the amount of carbamyl chloride present in the system after the tube had been in the water-bath at  $100^\circ$  for 5 minutes. This expression was used to obviate the initial disturbances.

### Results.

In Table I, where the results for methyl and *n*-propyl alcohols are given in detail, the first column gives the duration of heating in minutes ( $t$ ), the second the amount of hydrogen chloride present, expressed as c.c. of *N*/10-solution ( $b$ ), the third the amount of hydrogen chloride plus phenylmethylcarbamyl chloride present, expressed as c.c. of *N*/10-solution ( $c$ ). The fourth column gives the amount of phenylmethylcarbamyl chloride present ( $d$ ), obtained by subtracting the figures in column 2 from those in column 3. The fifth column gives the velocity coefficient for the reaction between phenylmethylcarbamyl chloride and the hydroxy-compound, calculated from the figures in column 4.

The whole of the results are summarised in Table II.

TABLE I.

<i>Methyl Alcohol.</i>					<i>n-Propyl Alcohol.</i>				
<i>t.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>k.</i>	<i>t.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>k.</i>
5	12.44	23.52	11.00	—	5	1.46	25.02	23.56	—
6	13.83	22.57	8.74	0.237	10	3.96	24.90	20.94	0.0236
8	14.96	20.59	5.63	0.216	15	6.49	24.71	18.22	0.0257
10	15.05	18.61	3.56	0.227	20	8.14	24.48	16.34	0.0244
13	14.18	16.18	2.00	0.214	25	9.81	24.11	14.30	0.0250
15	13.06	14.34	1.28	0.216	35	11.98	23.15	11.17	0.0249
			Mean	0.222	45	13.76	21.96	8.20	0.0264
					60	14.74	20.47	5.73	0.0257
								Mean	0.0251

TABLE II.

Hydroxy-compound.	Limits of <i>k.</i>	Mean <i>k.</i>
CH <sub>3</sub> .OH	0.237—0.214	0.222
C <sub>2</sub> H <sub>5</sub> .OH	0.0437—0.0417	0.0427
<i>n</i> -C <sub>3</sub> H <sub>7</sub> .OH	0.0264—0.0236	0.0251
<i>iso</i> -C <sub>3</sub> H <sub>7</sub> .OH	0.0113—0.0099	0.0106
<i>n</i> -C <sub>4</sub> H <sub>9</sub> .OH	0.0188—0.0166	0.0177
<i>iso</i> -C <sub>4</sub> H <sub>9</sub> .OH	0.0158—0.0154	0.0156
<i>iso</i> -C <sub>5</sub> H <sub>11</sub> .OH	0.0125—0.0121	0.0123
CH <sub>3</sub> .Ph.OH	0.0198—0.0179	0.0185
CH <sub>3</sub> .CH.CH <sub>3</sub> .OH	0.0448—0.0399	0.0420
CHPh.CH.CH <sub>3</sub> .OH	0.0078—0.0068	0.0074
PhOH	0.317—0.290	0.308
<i>o</i> -C <sub>6</sub> H <sub>4</sub> .Me.OH	0.0567—0.0514	0.0541
<i>m</i> -C <sub>6</sub> H <sub>4</sub> .Me.OH	0.149—0.139	0.146
<i>p</i> -C <sub>6</sub> H <sub>4</sub> .Me.OH	0.176—0.169	0.175
C <sub>6</sub> H <sub>5</sub> (OH) <sub>2</sub>	Too fast to measure accurately.	
C <sub>6</sub> H <sub>5</sub> (OH) <sub>3</sub>	Did not dissolve the carbamyl chloride.	

The hydroxy-compound may influence the reaction in two ways : by its constitution and by its solvent action. The influence of a solvent on the velocity of a reaction in which it does not take part has been extensively studied, and no general relation has been traced between the chemical or physical properties of the solvent and its effect on the velocity coefficient.

Menschutkin (*Z. physikal. Chem.*, 1887, 1, 611; 1890, 6, 41) found that the velocity of certain reactions was greatest in those solvents having the highest dielectric constant, but in other reactions this rule did not hold. Patterson and Montgomerie (*J.*, 1912, 101, 26, 2100) state that a given set of solvents may hasten a particular reaction in a certain sequence, whilst it may retard another reaction in the same or nearly the same sequence, and that the properties which bring this about are probably the same throughout.

Another view of the influence of the solvent is that the solvent and the solute form an unstable additive compound, in which case it is probable that the chemical constitution of the solvent, rather than its physical properties, would be most effective in influencing the velocity of the reaction. The work of Cox (*J.*, 1920, 117, 493) supports this view.

In the present work, the hydroxy-compound, which can be regarded as a solvent, reacts with the carbamyl chloride, hence its chemical constitution does influence the velocity of the reaction and the question arises whether, in addition to that, the physical properties of the hydroxy-compound play a part. The physical properties most likely to have some effect upon the velocity of a reaction are the viscosity, the dielectric constant, and the refractive index.

Reformatsky (*Z. physikal. Chem.*, 1891, 7, 34) showed that viscosity did not appear to have any great influence on the velocity coefficient of a reaction. The refractive index of the hydroxy-compounds examined varies between  $n_D^{20}$  1.3290 for methyl alcohol and  $n_D^{20}$  1.576 for cinnamyl alcohol; for most of them it is about 1.4, so that the small differences in refractive index are not sufficient to explain the large differences in velocity coefficient. The dielectric constant shows a greater variation, the highest being 32 for methyl alcohol (20°) and the lowest 9.7 for phenol (48°). These two extremes, however, are the values for the hydroxy-compounds having the greatest velocity coefficients, so that there does not seem to be a connexion between dielectric constant and velocity coefficient. In addition, the differences between the physical properties of the various liquids will tend to become smaller as the temperature is raised and therefore it is probable that at 100° the effect due to the different solvent action of the hydroxy-compounds will be very

small compared with the effect of their differences in chemical constitution.

In considering the effect of chemical constitution upon the velocity of a reaction several factors have to be taken into account: first, the general polar effect, due to substituent atoms or groups affecting the molecule as a whole; secondly, the steric effect; and thirdly, an alternate polarity effect. In many cases two or all three factors may operate simultaneously, and then it is difficult to assess the effect of each factor individually. With regard to the straight-chain aliphatic primary alcohols, the steric factor is not sufficiently strong to influence the velocity, and the results show no trace of an alternate effect, for the velocity coefficients are in the order methyl alcohol > ethyl alcohol > *n*-propyl alcohol > *n*-butyl alcohol. The order is the same as that found by Menshutkin (*Z. physikal. Chem.*, 1887, 1, 611) in the reaction between acetic anhydride and several alcohols in benzene solution at 100°, and different from that found by Norris and Ashdown (*loc. cit.*), where the order was methyl alcohol > ethyl alcohol > *n*-butyl alcohol > *n*-propyl alcohol. The reactivity of the alcohol decreases, *i.e.*, the hydroxyl hydrogen atom becomes more firmly bound, as the length of the straight chain increases. With the primary *iso*-compounds it is again seen that an extra  $-\text{CH}_2-$  group in the straight chain decreases the velocity coefficient. A branched-chain alcohol has a smaller velocity coefficient than a straight-chain alcohol of the same molecular weight; thus *n*-propyl > *isopropyl* and *n*-butyl > *isobutyl*. In the case of *isopropyl* alcohol the velocity coefficient is abnormally small, probably owing to a steric effect superimposed upon the general polar effect of the substituent, since this is a secondary alcohol whilst the others are primary alcohols. A similar effect was found by Ashdown and Norris.

The introduction of a phenyl group at the end of the straight chain decreases considerably the reactivity of the alcohol, as is shown by the following figures: methyl alcohol 0.222, benzyl alcohol 0.0185, allyl alcohol 0.0420, cinnamyl alcohol 0.00744.

The effect of unsaturation is to cause a great increase in the reactivity of the alcohol; thus *n*-propyl alcohol 0.0251, allyl alcohol 0.0420.

Taking methyl alcohol as the standard, and considering the replacement of one of its hydrogen atoms in the methyl group, we find that the general polar effect of the various substituents in decreasing the reactivity of the hydroxyl hydrogen is in the following order:  $\text{CH}_3 < \text{CH}_2\cdot\text{CH} < \text{C}_2\text{H}_5 < \text{C}_6\text{H}_5 < \text{C}_3\text{H}_7 < \text{CH}(\text{CH}_3)_2 < \text{CH}(\text{CH}_3)_2\cdot\text{CH}_2 < \text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}$ .

The introduction of a second hydroxyl group, as in ethylene

glycol, increases the reactivity so greatly that the velocity coefficient cannot be obtained with accuracy by the method employed.

The aromatic compounds show special features. Phenol, as was to be expected, is very reactive, more so than methyl alcohol. The introduction of a methyl group, as in the cresols, diminishes the reactivity of the hydroxyl hydrogen, the extent of the diminution depending on the relative positions of the methyl and hydroxyl groups in the benzene ring. The velocity coefficients are: phenol 0.308, *o*-cresol 0.0541, *m*-cresol 0.146, *p*-cresol 0.175. The low value for *o*-cresol is undoubtedly due to a preponderating steric effect.

Work with other carbamyl chlorides is in progress.

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## XCI.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXVIII. d-sec.-Butylbenzene.*

By PHILIP WILLIAM BENSON HARRISON, JOSEPH KENYON,  
and JOHN ROBERT SHEPHERD.

OF the compounds which have been examined in the study of the relationship between chemical constitution and optical activity, very few have been hydrocarbons, probably because of the experimental difficulties in preparing this type of compound in an optically active condition.

Mention may be made, however, of *d*-methylethyl-*n*-propylmethane with  $[\alpha]_D^{20} + 9.5^\circ$ , which was prepared by Marckwald (*Ber.*, 1904, 37, 1046) by the action of sodium on a mixture of ethyl iodide and *d*-amyl iodide. Klages and Sautter (*Ber.*, 1904, 37, 649) prepared *d*- $\alpha$ -phenyl- $\gamma$ -methylpentane ( $[\alpha]_D^{18} + 17.2^\circ$ ) by the reduction of *d*- $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta^a$ -pentene ( $[\alpha]_D^{18} + 43^\circ$ ), which was obtained by the interaction of active amyl iodide ( $[\alpha]_D^{18} + 5.78^\circ$ ) and benzaldehyde in presence of magnesium. The same authors (*Ber.*, 1905, 38, 2312), by analogous reactions, prepared *d*- $\gamma$ -*m*-isopropylphenyl- $\gamma$ -methylpentane ( $[\alpha]_D^{18} + 15.91^\circ$ ) and *d*- $\gamma$ -*m*-isopropylphenyl- $\gamma$ -methyl- $\Delta^a$ -pentene ( $[\alpha]_D^{18} + 41.89^\circ$ ).

This communication describes the preparation of *sec*-butylbenzene in what is believed to be an optically pure condition.



The preparation has proved to be so tedious and laborious that the question of preparing other optically active hydrocarbons will be held in abeyance until a more convenient procedure has been devised.

The method of preparing *d*-*sec*.-butylbenzene is briefly as follows : The inactive hydrocarbon was nitrated and the *p*-nitro-*sec*.-butylbenzene, which is the principal product of the reaction, was reduced to *p*-amino-*sec*.-butylbenzene. The latter was then converted into the *hydrogen tartrate*, which was submitted to systematic prolonged fractional crystallisation until a salt of constant rotatory power was obtained. The amino-group of the optically active base obtained by the decomposition of this salt was then eliminated in the usual way, giving optically active *sec*.-butylbenzene.

The resolution of *sec*.-butylbenzene into its optically active isomerides had been attempted previously. Klages (*Ber.*, 1906, 39, 2131) converted the hydrocarbon into its sulphonic acid and obtained therefrom a number of crystalline salts by combining it with several of the commoner alkaloids. Fractional crystallisation of these salts, however, brought about no resolution.

*p*-Amino-*sec*.-butylbenzene was obtained in an optically active condition by Glattfeld and Wertheim (*J. Amer. Chem. Soc.*, 1921, 43, 2682) by the crystallisation of the salt with *d*-camphorsulphonic acid. The rotatory power of the amine quoted by these authors is, however, far too low, being some sixty times smaller than the value obtained in the course of the present work.

Each of the compounds now described exhibits a very high optical rotatory dispersive power:  $\alpha_{4359}/\alpha_{5461} = 1.87$  for the amine and 1.81 for the hydrocarbon, whilst an examination of the rotatory powers shows that in no case do they satisfy the simple dispersion equation  $\alpha = K/(\lambda^2 - \lambda_0^2)$ .

As it is possible that the high optical rotatory dispersive power may be due to these compounds containing a benzene nucleus in the molecule, several attempts were made to reduce *sec*.-butylbenzene to *sec*.-butylcyclohexane to ascertain what effect, if any, the loss of aromatic character would have on the rotatory dispersive power. However, under the conditions employed, namely, agitation of the substance with hydrogen in the presence of colloidal platinum or palladium, little, if any, reduction was effected.

#### EXPERIMENTAL.

*dl*-*sec*.-Butylbenzene was prepared by the method of Klages (*Ber.*, 1902, 35, 2641). The methylethylphenylcarbinol obtained by the interaction of magnesium ethyl chloride and acetophenone was slowly distilled at the ordinary pressure, and the resulting

$\beta$ -phenyl- $\Delta^2$ -butylene (75% yield) reduced rapidly with sodium and absolute alcohol. *sec*-Butylbenzene was collected at 168—173° and obtained in 87% yield.

*p*-Nitro-*sec*-butylbenzene.—To *dl*-*sec*-butylbenzene (200 g.) was added during 3 hours a mixture of nitric acid (128 c.c.; *d* 1.42) and sulphuric acid (160 c.c.; *d* 1.84) at such a rate that the temperature of the reaction was maintained at 15—20°; external cooling was resorted to, and the mixture kept vigorously stirred. The principal product of the reaction was *p*-nitro-*sec*-butylbenzene—shown by the production of *p*-nitrobenzoic acid in good yield on oxidation—accompanied by a relatively small amount of a lower-boiling fraction which was presumably *o*-nitro-*sec*-butylbenzene. Only a rough separation was possible at this stage, owing to the difficulty of obtaining a fraction of constant boiling point. Further purification was, however, easily effected after the next operation by the recrystallisation of the *oxalates* of the mixed amines.

*dl*-*p*-Amino-*sec*-butylbenzene.—The *p*-nitro-compound was very easily reduced to the corresponding amine by tin and concentrated hydrochloric acid. After decomposition of the stannic chloride compound of the base by caustic soda, the amine was isolated by distillation in steam.

The mixture of neutral *oxalates* of the amines was crystallised several times from hot water and it was found by determining the density of the amine recovered that one crystallisation was sufficient to remove almost completely the lower-boiling isomeride of greater density. The amine thus obtained distilled constantly at 118°/15 mm.; its density (*d*<sub>4</sub><sup>25</sup> 0.949), and the melting point (123°) of its acetyl derivative were unaltered after further recrystallisation of the neutral *oxalate*. Reilly and Hickinbottom (J., 1920, 117, 120) give 125—126° as the melting point of *p*-*sec*-butylacetanilide; that prepared by the present authors melts at 123° even after several recrystallisations.

*Resolution of dl-p-Amino-sec-butylbenzene*.—Salts of the *dl*-amino with several optically active acids were prepared—that with *l*-malic acid was excessively soluble and could not be crystallised; those with *d*-camphoric and *d*-camphorsulphonic acids were crystalline, but their separation into enantiomorphous forms by fractional crystallisation was too slow to be of use. The compound with *d*-hydroxymethylenecamphor was also prepared, but fractional crystallisation of this failed to effect any resolution. (This is in agreement with the observation of Glattfeld and Wertheim, *loc. cit.*).

After many preliminary attempts it was found that the *d*-hydrogen

tartrate was the most promising of all the salts tried. *p*-Amino-*sec*.-butylbenzene (285 g.) was added to a hot solution of *d*-tartaric acid (300 g.) in water (1100 c.c.); the clear solution on standing deposited a crop of crystals (which titration showed to be the *hydrogen tartrate*) in very small, prismatic rods. These were systematically recrystallised until the rotatory power of the amine obtained by decomposing successive crops of the crystals became constant. The rate of the resolution is indicated by the following data :

After four recrystallisations of the hydrogen tartrate, the observed rotatory power ( $\alpha_{5461}^{20}$ ;  $l = 100$  mm.) of the liberated base was  $+16^\circ$ , after eight  $+23^\circ$ , after twelve  $+28^\circ$ , after sixteen  $+31^\circ$ , after twenty-two  $+37^\circ$ , after twenty-five  $+38.2^\circ$ , after twenty-seven  $+38.7^\circ$ , after thirty  $+38.7^\circ$ .

This prolonged process of recrystallisation is very wasteful and the *d-p*-amino-*sec*.-butylbenzene obtained by decomposition of the various crops of salt of constant rotatory power amounted to only 10 g. The amine had b. p.  $114^\circ/12$  mm. and  $d_4^{20} 0.945$ .

Various attempts were made to isolate the *l*ævorotatory form of *p*-amino-*sec*.-butylbenzene in an optically pure condition, but without success. By the decomposition of the most soluble fractions of the hydrogen tartrate, portions of amine of rotatory powers lying between  $\alpha_{5461} - 12^\circ$  and  $-20^\circ$  were obtained. The *d*-camphorsulphonate of the base with  $\alpha_{5461} - 20^\circ$  was prepared and recrystallised several times; the *l*ævorotation of the amine obtained from the less soluble fractions of this salt increased, but at so slow a rate as to render the method valueless. Recrystallisation of the hydrochloride and of the oxalate of the partially active amine was also without effect on the rotatory power. Other solvents besides water were tried in all the above bases for recrystallisation of the various salts, but they bring about separation with even greater slowness than does water.

*d-sec*.-Butylbenzene was readily prepared by mixing a solution of *d-sec*.-butylbenzenediazonium chloride (from 6 g. of amine) with a strongly alkaline solution of sodium stannite and distilling the mixture in a current of steam. The hydrocarbon was obtained as a colourless liquid which distilled constantly at  $172^\circ$ ; the yield was 2 g. = 40% of the theoretical (compare Friedländer, *Ber.*, 1889, 22, 587).

Although it was considered unlikely that any racemisation would occur during the elimination of the amino-group situated at the end of the molecule remote from the asymmetric carbon atom, yet the following experiments were carried out to gain some information on this important point. Partially active *d*- and *l-p*-amino-*sec*.-butylbenzenes of various degrees of rotatory power were diazotised

*Determinations of Rotatory Power.*

d-p-Amino-sec.-butylbenzene.  $\alpha_D^{20}$  0.9449.

Solvent.	Gt. of solute in 100 c.c. of soln.	l in mm.	$\alpha_D^{20}$ Observed.		$[\alpha]_D^{20}$ .	
			$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .
Homogeneous .....	—	25	6708.	5896.	5790.	4359.
Ethyl alcohol .....	4.94	100	+5.85°	+8.00°	+8.37°	+9.68°
Carbon disulphide ...	5.01	100	1.31	1.76	—	+18.10°
Chloroform .....	5.02	100	1.45	2.00	2.05	+33.86°
			1.15	1.63	1.72	26.5
					2.44	35.6
					2.00	28.9
					3.72	39.9
					22.9	32.5
					34.3	41.5
					39.8	48.7
					74.1	99.0
Chloroform .....	4.99	100	0.97	1.34	1.40	1.58
					2.90	26.8
					31.6	58.1
Homogeneous .....	—	25	4.41	5.90	6.19	7.14
					12.96	20.42
					27.31	28.66
					33.15	60.0

d-p-sec.-Butylacetamide. M. p. 124°.

d-sec.-Butylbenzene.  $\alpha_D^{20}$  0.8639.

Solvent.	Gt. of solute in 100 c.c. of soln.	l in mm.	Density.		Refractive Index ( $n_D^{20}$ ).	
			$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .
d-sec.-Butylbenzene .....	—	25	0.8681,	0.8639,	1.4838	1.4890
d-p-Amino-sec.-butylbenzene .....	—	25	0.9475,	0.9440,	1.4883	1.4915
dl-p-Nitro-sec.-butylbenzene .....	—	25	1.063.	—	1.5284	1.5391
					—	1.5322
					5896.	5461.
					5790.	4359.
					1.4890	1.5061
					1.5356	1.5589
					1.5363	1.5622

and treated with sodium stannite under different experimental conditions; the ratio of the rotatory power of the original amine to that of the hydrocarbon obtained from it in each of the several cases was quite constant, thus rendering it highly improbable that any racemisation had taken place.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant with which some of the materials used in this investigation were purchased. Two of them (J. R. S. and P. W. B. H.) wish also to acknowledge their indebtedness to the Department of Scientific and Industrial Research for maintenance grants which enabled them to participate in the work.

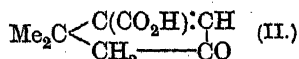
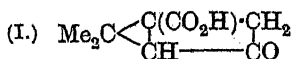
BATTERSEA POLYTECHNIC,  
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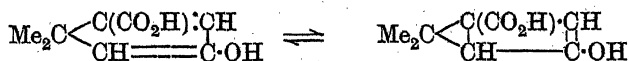
## XCII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides.* *Part VI. Some Reactions of isoPhorone.*

BY JOHN WILLIAM BAKER.

THE chemistry of homocyclic compounds is often complicated by reactions which find no simple explanation in the structure usually assigned to the compound (Farmer and Ingold, J., 1920, **117**, 1362, and subsequent papers), the ambiguity extending in one case even to the synthesis of the substance, syntheses which should yield respectively the acids (I) and (II) yielding the same acid (Farmer, Ingold, and Thorpe, J., 1922, **121**, 128).



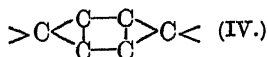
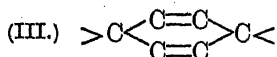
Such conflicting evidence was reconciled by the assumption of intra-annular tautomerism between the *bicyclopentene* and the *cyclopentadiene* systems, the two enolic forms being merely valency isomerides in accordance with the scheme :



There is no *a priori* reason why such redistribution of residual affinity within the ring, extending from mere conjugation of affinity across the ring to the establishment of a real bridge bond, should be restricted to the *cyclopentadiene* series: its extension to the

heterocyclic rings thiophen and furan, and to benzene has already been developed (Ingold, J., 1922, 121, 1133, and subsequent papers).

The present paper deals with the extension of such intra-annular tautomerism to the *cyclohexadiene* series in accordance with the general scheme :



On first inspection it may be considered that the structure (IV) is improbable in view of the strain involved, but it must be understood that it is not intended to represent a stable individual substance, but merely a phase in the scheme of valency distribution which, under favourable conditions, may pass into a more stable, true bridged phase. Such favourable conditions may occur when one or both of the potential trimethylene rings are stabilised by the presence of a *gem*-dimethyl group, and, in this case, products containing a *cyclopropane* ring may result from the degradation of the molecule.

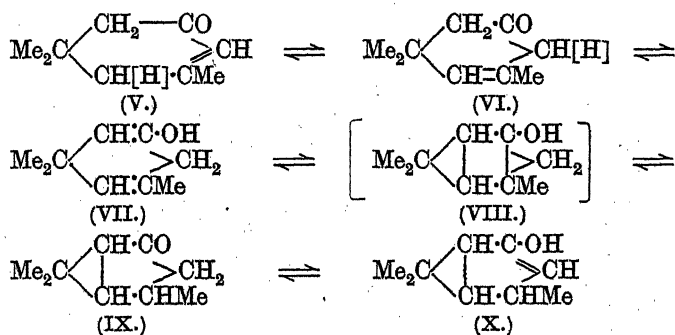
An example of this type of intra-annular tautomerism has, in the author's opinion, been established in the case of *isophorone*. The generally accepted formula (V) for *isophorone* has been established both by synthesis and by oxidation. Knoevenagel and Fischer (*Annalen*, 1897, 297, 185) obtained it by the condensation of mesityl oxide and ethyl acetoacetate at 5° and hydrolysis of the *isophorone*carboxylic ester so produced. The structure was confirmed by Crossley and Gilling (J., 1909, 95, 24), who obtained the ketone by the condensation of ethyl sodiomalonate with chloro-dimethyl*cyclohexenone* and hydrolysis of the ethyl dimethyl*cyclohexenone*acetate so obtained.

The oxidation of *isophorone* was investigated by Bredt and Rubel (*Annalen*, 1898, 299, 160), who obtained a whole series of acids intermediate between *isophorone* and its final oxidation product, *as*-dimethylsuccinic acid. Formula (V) is also in good accord with most of the reactions of the ketone, *e.g.*, the formation of monobenzylidene-monopiperonylidene derivatives.

Kerp and Muller (*Annalen*, 1898, 299, 193), however, found that this structure alone was not sufficient to represent all the reactions of *isophorone* (obtained, in this case, by the condensation of acetone). *isoPhorone* condenses with another molecule of acetone to yield a higher condensation product, xylitone, which these investigators found also yields a monobenzylidene derivative, and hence must contain the group  $CMe_2:C \cdot CO \cdot CH_2 \cdot$ ; this necessarily involves the existence of the group  $\cdot CH_2 \cdot CO \cdot CH_2 \cdot$  in the original *isophorone* molecule. Hence, in this reaction at least, *isophorone*

must be represented by the structure (VI) rather than (V), and these authors concluded that *isophorone* obtained from acetone is a static mixture of the two isomerides (V and VI).

The interconversion of these two forms merely involves the well-known  $\alpha\beta$ - $\beta\gamma$  change across a three-carbon system, and the conflicting results would be readily explained if such a tautomeric system were assumed to exist in the *isophorone* molecule. The enolic modification (VII) of the structure (VI) conforms to the *cyclohexadiene* type mentioned above, and hence there is the possibility of a second kind of tautomeric change, *viz.*, intra-annular, a redistribution of affinity across the ring resulting, initially, in the *tricyclohexane* structure (VIII). It is not suggested that this form represents more than a transitory phase in the whole scheme, for only one of the potential three-membered rings is stabilised by the presence of a *gem*-dimethyl group, and it is to be expected that such a structure would immediately ketonise across the ring, thus destroying the unstabilised three-membered ring, to yield a bridged modification of the *isophorone* molecule (IX). Finally, this could change in the usual manner to yield an enolic modification of a bridged form of *isophorone*. The complete scheme is as follows :

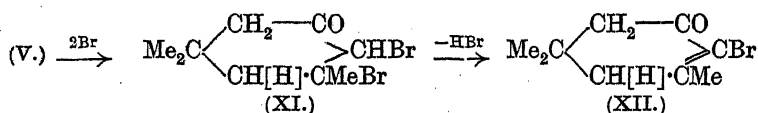


Thus in the *isophorone* molecule three types of tautomerism are possible, each being superimposed on the other; (a) three-carbon,  $\alpha\beta$ - $\beta\gamma$ -change, (b) intra-annular, (c) keto-cyclol.

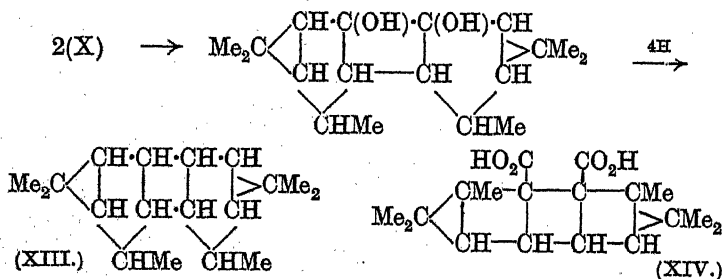
Evidence is submitted in this paper which, in the author's opinion, can be explained only by assuming such a scheme in connexion with the *isophorone* molecule.

Kerp and Muller (*loc. cit.*) found that in ice-cold glacial acetic acid solution *isophorone* forms an unstable dibromo-additive product which spontaneously evolves hydrogen bromide. Their analysis is 5% low for this compound. When, however, *isophorone* in ice-cold carbon tetrachloride solution is treated with a standard

solution of bromine in the same solvent, absorption is rapid and a white, crystalline dibromo-compound (XI) separates, but no trace of hydrogen bromide is evolved until two atoms of bromine have been added. This additive compound is stable in the absence of moisture, but on exposure to air it immediately loses one molecule of hydrogen bromide to form monobromoisophorone (XII). Although the possibility of bromine addition to the enolic double bond and subsequent loss of hydrogen bromide to yield a  $\alpha$ -bromoketone cannot be excluded, it is considered more probable, in view of the degree of stability of the intermediate compound, that the addition of bromine occurs at the double bond in the three-carbon system, thus forming a blocked system, which therefore spontaneously liberates hydrogen bromide to reform a mobile system in accordance with the scheme :



Evidence of the bridged modification of *isophorone* was obtained by a study of its reduction products. When *isophorone* is reduced by the Clemmensen method, a solid hydrocarbon,  $\text{C}_{18}\text{H}_{28}$ , can be isolated in small yield from the product. This hydrocarbon is saturated, and therefore valency considerations necessitate the existence of the bridged structure (XIII). This structure is supported by the oxidation of the hydrocarbon with boiling potassium permanganate in sodium hydrogen carbonate suspension, the main product being *trans*-caronic acid. The formation of this hydrocarbon from the bridged, enolic modification of *isophorone* (X) is represented by the following scheme, additive ring formation preceding the reduction :

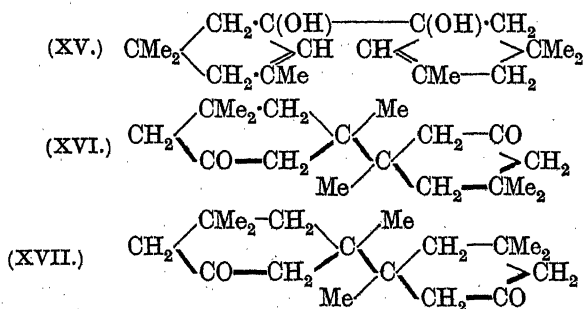


A similar constitution has been assigned to  $\alpha$ -dicamphylic acid (XIV) obtained by the action of potash on sulphocamphylic acid (Perkin, J., 1903, 83, 835).

Reduction of *isophorone* with sodium and moist ether yields a



mixture of two isomerides,  $C_{18}H_{30}O_2$ , m. p.  $126^\circ$  and  $162^\circ$ , respectively. The latter is undoubtedly the product obtained by Hess and Munderloh (*Ber.*, 1916, **51**, 383) by the reduction of *isophorone* with 2.5% sodium amalgam and methyl alcohol. These investigators, apparently merely on the analytical data, assigned the pinacol formula (XV) to this product. Such a constitution is, however, quite inconsistent with the properties of this reduction product. Both substances, m. p.  $126^\circ$  and  $162^\circ$ , are saturated and do not decolorise potassium permanganate in sodium hydrogen carbonate solution in the cold, both yield disemicarbazone derivatives, but neither will form an acetyl derivative on heating with acetic anhydride. They are probably derived from the unsaturated ring form of *isophorone* (VII) by a reduction similar to that which occurs in the formation of deoxymesityl oxide and deoxyphorone, respectively, from mesityl oxide and phorone, two stereoisomerides (XVI and XVII) being produced.



Thus the ambiguity of structure which had previously been noted in the *cyclopentadiene* series would seem to be present also in other unsaturated cyclic systems, and may indeed be of much more frequent occurrence than is generally supposed.

#### EXPERIMENTAL.

The *isophorone* employed was prepared by the condensation of mesityl oxide and ethyl acetoacetate (Knoevenagel and Fischer, *loc. cit.*), but at the temperature of the steam-bath for 4 hours, under which conditions the main portion of the *isophorone*carboxylic ester is converted into *isophorone*. The fraction, b. p.  $95\text{--}100^\circ/14$  mm., consisted of nearly pure *isophorone*. In order to determine whether it was a single individual or a mixture of isomerides (compare Kerp and Muller, *loc. cit.*), its semicarbazone was submitted to a rigorous fractional crystallisation from alcohol. No trace of a second semicarbazone could be detected. The pure semicarbazone, crystallised from alcohol, has m. p.  $199.5^\circ$  (decomp.) (Crossley and

Gilling, *loc. cit.*, give  $191^{\circ}$ ), and does not depress the melting point of a specimen prepared by the latter method (Found: C, 61.5; H, 8.8. Calc., C, 61.5; H, 8.8%). The ketone regenerated from the pure semicarbazone by steam distillation with oxalic acid had b. p.  $99^{\circ}/14$  mm.; the oxime had m. p.  $79.5^{\circ}$  (Crossley and Gilling, *loc. cit.*, give  $78^{\circ}$ ).

A *monopiperonylidene* derivative was obtained and after crystallisation from ethyl acetate had m. p.  $145\text{--}146^{\circ}$  (Found: C, 75.2; H, 7.0.  $C_{17}H_{18}O_3$  requires C, 75.4; H, 6.7%).

*Bromination of isoPhorone. Formation of the Unstable Dibromide (X).*—A standard solution of dry bromine in dry carbon tetrachloride (1 c.c. = 0.1 g. Br) was added dropwise to a solution of 1 g. of dry *isophorone*, in a little carbon tetrachloride cooled in ice, moisture being rigorously excluded. Decoloration was instantaneous, and when 2 c.c. had been added the crystalline dibromide began to separate. When 13 c.c. (1.3 g. Br) had been added, the solution became coloured with free bromine and a trace of hydrogen bromide could be detected. Addition of two atoms of bromine requires 1.2 g. of bromine. After traces of bromine and hydrogen bromide had been removed under diminished pressure, the product was broken into a large excess of water, and the liberated hydrobromic acid titrated with potassium hydroxide (Found: 0.56 g. of hydrogen bromide. Liberation of 1 mol. of hydrogen bromide requires 0.60 g.). In another experiment the solvent was removed by evaporation in a vacuum. The dibromide remained as a mass of short, thick prisms, m. p. about  $40^{\circ}$ , which on exposure to air immediately changed to a colourless oil with the evolution of hydrogen bromide.

*Monobromoisophorone (XII).*—The carbon tetrachloride solution of the unstable dibromide having been poured into water, the precipitated, colourless oil was extracted with pure ether and washed with very dilute alkali. The residue from the dried ethereal extract was left in an evacuated desiccator over potash for 24 hours, and since it could not be distilled without decomposition, was analysed in the crude state (Found: C, 50.4; H, 6.2.  $C_9H_{18}OBr$  requires C, 49.8; H, 6.0%).

1 : 3 : 4 : 5 (?) - *Tetrabromo-3 : 3 : 5-trimethylcyclohexan-1-one* is obtained by exhaustive bromination of *isophorone* in carbon tetrachloride solution. After crystallisation from ethyl acetate-ligroin (b. p.  $60\text{--}80^{\circ}$ ), it has m. p.  $135^{\circ}$  (Found: C, 24.0; H, 2.4; Br, 70.7.  $C_9H_{12}OBr_4$  requires C, 23.7; H, 2.6; Br, 70.2%). The same compound is produced when an excess of bromine is added to *isophorone* in ice-cold glacial acetic acid solution, and crystallises on keeping.

Attempts to prepare the tribromo-compound always resulted in the formation of an uncrystallisable gum.

*Reduction of isoPhorone.*—(1) *With sodium and moist ether.* *Formation of 1:1':3:3:3':3':3'-trimethylbicyclohexyl-5:5'-dione*,  $\alpha$  and  $\beta$  forms (XVI and XVII). *isoPhorone* was dissolved in 20–30 times its volume of ether saturated with water, and sodium wire added in small successive portions. It seems to be essential to allow the first reaction to proceed as vigorously as possible. A flocculent solid separated, the liquid turning first yellow and finally deep red. The product was poured into water, acidified with hydrochloric acid, extracted with ether, and any acid fraction removed with sodium hydrogen carbonate solution. The neutral residue was a brown syrup which partly crystallised. The solid crystallised from ethyl acetate–ligroin had m. p.  $162^{\circ}$  (Found: C, 77.6; H, 10.8; *M*, cryoscopic in benzene, 268.  $C_{18}H_{30}O_2$  requires C, 77.6; H, 10.8%; *M*, 280). It does not decolorise potassium permanganate in sodium hydrogen carbonate solution.

A *disemicarbazone* was obtained which after crystallisation from glacial acetic acid had m. p.  $259\text{--}260^{\circ}$  (decomp.) (Found: C, 61.0; H, 9.4.  $C_{20}H_{36}O_2N_6$  requires C, 61.2; H, 9.3%).

The portion of the reduction product which had failed to solidify was fractionally distilled under reduced pressure. Low fractions consisting mainly of unchanged *isophorone* were first obtained, and then a large, exceedingly viscous fraction distilled at  $220\text{--}240^{\circ}/20$  mm., which immediately solidified when rubbed with low-boiling ligroin. The solid was crystallised from ethyl acetate–ligroin. It consists of the second isomeride, m. p.  $126^{\circ}$  (Found: C, 77.4; H, 10.7%). It does not decolorise potassium permanganate in sodium hydrogen carbonate solution in the cold, and only slowly on boiling. Careful fractional crystallisation of this substance failed to indicate the presence of any other product. A further quantity of this isomeride was obtained by a second fractional distillation of the gum obtained from the ligroin mother-liquors.

A *disemicarbazone* was obtained as before, but was precipitated from the alcoholic reaction mixture only on addition of water. After crystallising several times from about 90% methyl alcohol, it had m. p.  $220^{\circ}$  (decomp.) (Found: C, 61.2; H, 9.4%).

The same products were obtained when *isophorone* was reduced with zinc and acetic acid, or with sodium amalgam and a boiling alkaline solution.

(2) *By the Clemmensen method.* *Formation of the hydrocarbon* (XIII). The ketone (10 g.) was refluxed with about 50 g. of amalgamated zinc and an excess of concentrated hydrochloric acid for 3 hours, small quantities of hydrochloric acid being occasionally

added. The reaction mixture was steam distilled. The first portion of the distillate consisted of a very small quantity of a volatile oil, with a camphoraceous odour, which was not obtained in quantity sufficient for identification. The hydrocarbon then distilled and solidified in the receiver, cooled in ice. The yield was small, a large amount of resinous material, non-volatile in steam, being produced. The hydrocarbon was extracted with ether, and the residue from the dried extract rapidly solidified. It crystallised from dilute alcohol in fine needles, m. p.  $112^{\circ}$  (Found : C, 88.5; H, 11.5;  $M$ , cryoscopic in benzene, 231.  $C_{18}H_{28}$  requires C, 88.5; H, 11.5%;  $M$ , 244). It is stable to potassium permanganate in sodium hydrogen carbonate solution in the cold, but decolorises bromine in carbon tetrachloride solution, probably owing to the destruction of two of the bridge bonds.

*Oxidation of the Hydrocarbon XIII.*—The hydrocarbon (0.42 g.), suspended in a solution of potassium permanganate and sodium hydrogen carbonate, was heated under reflux, successive quantities of permanganate being added until the reaction mixture remained pink (48 hours). The product was steam-distilled to remove traces of the hydrocarbon, and the alkaline liquor was worked up in the usual manner, acidified at  $0^{\circ}$  with dilute sulphuric acid, and the product extracted with pure ether. The residue from the dried, ethereal extract immediately solidified. Crystallised from pure ether, it had m. p.  $212-213^{\circ}$ , either alone or mixed with a genuine specimen of *trans*-caronic acid (Found, by micro-combustion : C, 52.6; H, 6.7. Calc., C, 53.1; H, 6.4%). The oxidation was repeated, with the same result, on a fresh quantity of the hydrocarbon obtained by the reduction of a different specimen of isophorone.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant with which the expenses of this research were met, and to Professor C. K. Ingold, F.R.S., for his continued interest and valuable suggestions during the progress of the investigation.

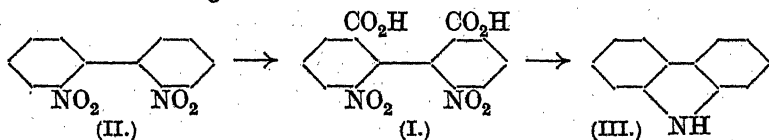
THE UNIVERSITY, LEEDS.

[Received, December 22nd, 1925.]

XCIH.—*The Molecular Configurations of Polynuclear Aromatic Compounds. Part VI.  $\beta$ -Dinitrodiphenic Acid; its Constitution and Resolution into Optically Active Components.*

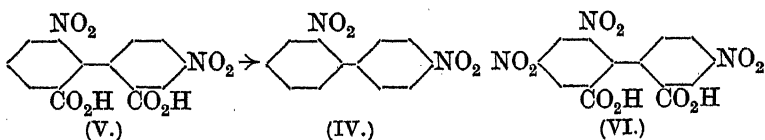
By GEORGE HALLATT CHRISTIE, ALBERT HOLDERNESS, and JAMES KENNER.

$\beta$ -DINITRODIPHENIC acid, originally obtained by Schultz (*Annalen*, 1880, 203, 108), is prepared by oxidation of the dinitroquinone produced, with its 2:7-isomeride, when phenanthraquinone is dinitrated. This acid has been regarded as a 6:6'-dinitrodiphenic acid (I) since it was examined by Schmidt and Kämpf (*Ber.*, 1903, 36, 3745), who claimed to have converted it by distillation with dry sand into 2:2'-dinitrodiphenyl (II). "Wir erhielten dabei sehr wenig eines schwer löslichen Körpers vom Schmelzpunkt ca. 240° (wahrscheinlich Dinitrofluorenon) und als Hauptproduct ca. 1 g. einer leichter löslichen Verbindung vom Schmelzpunkt 124–6° Dieselbe wurde genau verglichen mit o-o'-Dinitrodiphenyl, das wir uns nach den Angaben von Ullmann (*Ber.*, 1901, 34, 3803) bereitet hatten. Beide Präparate zeigten in allen Eigenschaften völlige Uebereinstimmung."



The conversion of the corresponding diaminodiphenic acid into carbazole (III) recorded at the same time supplied confirmatory, though obviously less conclusive, evidence in support of the very precise statement quoted, so that Kenner and Stubbings (*J.*, 1921, 119, 593) felt justified in regarding their synthetic 6:6'-dinitrodiphenic acid as a stereoisomeride of Schultz's acid when it was found that the two differed in properties.

The observations recorded by Christie and Kenner (this vol., p. 470) rendered it necessary, however, to re-examine Schultz's acid. The outcome of our experiments, carried out under somewhat different conditions from those used by Schmidt and Kämpf, was that in place of 2:2'-dinitrodiphenyl, m. p. 124°, 2:4'-dinitrodiphenyl (IV), m. p. 93°, was obtained, so that Schultz's acid would be 4:6'-dinitrodiphenic acid (V):

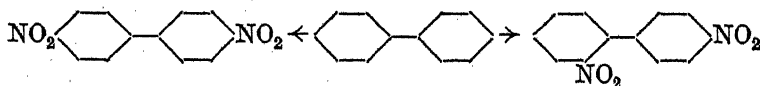


This result in itself is no more definite than that claimed by Schmidt and Kämpf, and perhaps somewhat less so if regard be paid to the considerably lower melting point of our product. Further, we were unable to detect any other product than 2:7-dinitrophenanthraquinone when 2-nitrophenanthraquinone was nitrated under the conditions for converting phenanthraquinone into 2:7- and what the above result would indicate to be 2:5-dinitrophenanthraquinones. The following considerations will, however, probably be held to be decisively in favour of our view rather than that of Schmidt and Kämpf:

(1) The same 2:4:7-trinitrophenanthraquinone is formed from the dinitroquinone in question and 2:7-dinitrophenanthraquinone, and attempts to prepare 2:4:5:7-tetranitrophenanthraquinone by further nitration have been unsuccessful (Christie and Kenner, *loc. cit.*).

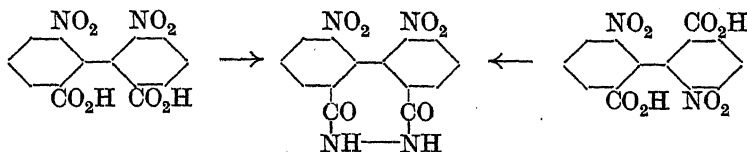
(2) It would be expected that if 4:5- and 2:7-dinitroquinones are produced from phenanthraquinone by nitration, some of the 2:5-isomeride also would be formed. But only two products have been observed.

(3) Dinitration of diphenyl furnishes the 2:4'- and 4:4'-derivatives as chief, if not sole products (Fittig, *Annalen*, 1862, 124, 276):



(4) The amino-group in 6-aminodiphenic acid is not diazotisable, but one of those in the diamino-acid, for which the 4:6'-constitution is now advocated, is diazotisable (Schmidt and Schall, *Ber.*, 1905, 38, 3769). In previous papers, it was shown that such 6-aminoacids readily form phenanthridone derivatives. The accounts in the literature of the acids referred to make it not impossible that they may in reality be phenanthridone derivatives, as has been shown to be the case with other compounds similarly derived (compare Christie and Kenner, *loc. cit.*).

Kenner and Stubbings (*loc. cit.*) converted their synthetic 6:6'-dinitrodiphenic acid into a "hydrazide," and suggested that this derivative might furnish a means of converting the new acid into its supposed stereoisomeride:



This idea gained further credence when a "hydrazide" was prepared from the  $\beta$ -acid, and behaved similarly when heated. However, the "hydrazides" from the two sources differed in their behaviour towards acetic anhydride and were readily converted by oxidative hydrolysis with fuming nitric acid according to a procedure very briefly indicated by Curtius and Foersterling (*J. pr. Chem.*, 1895, 51, 371), into acids melting, respectively, at  $300^\circ$  and  $249-253^\circ$ , as compared with  $300^\circ$  and  $258-259^\circ$  recorded for the original acids. Clearly, then, no interconversion of the acids is to be achieved through the hydrolysis of the "hydrazides" as intermediates.

$\beta$ -Dinitrodiphenic acid, if it is the 4:6'-derivative, is closely related in constitution to 4:6:4'-trinitrodiphenic acid (VI), of which the resolution into optically active components through the agency of brucine has been described (Christie and Kenner, *J.*, 1923, 123, 779).

Similar experiments with the  $\beta$ -acid showed that it furnished a uniform brucine salt, but on the other hand two distinct quinine salts were obtained which were easily separable owing to their different solubilities in alcohol. From these salts, solutions of optically active acids and their sodium salts were prepared in the usual manner. A second illustration is therefore provided of an acid capable of existence in an asymmetric form when only three of the four 2, 6, 2', and 6'-positions are occupied by substituents.

Since the stereoisomerism of  $\beta$ - and 6:6'-dinitrodiphenic acids, which originally inspired the experiments on their resolution, would now seem to be non-existent, it is perhaps desirable to record the fact that the resolution of the  $\beta$ -acid has been repeated with freshly prepared materials by Mr. V. M. Trikojus, B.Sc., in the laboratories of the University of Sydney.

#### EXPERIMENTAL.

$\beta$ -Dinitrodiphenic acid, prepared by Schmidt and Kämpf's method (*loc. cit.*), was further characterised by the preparation of its *chloride*, colourless, rectangular plates, m. p.  $120^\circ$ , from benzene-light petroleum (Found: N, 7.9.  $C_{14}H_6O_6N_2Cl_2$  requires N, 7.6%); its *ethyl ester*, colourless, pentagonal prisms, m. p.  $114-115^\circ$  (Found:

N, 7.3.  $C_{18}H_{16}O_8N_2$  requires N, 7.2%); and its *amide*, colourless, hexagonal prisms, m. p. 247.5°, from dilute alcohol (Found: N, 17.2.  $C_{14}H_{10}O_6N_4$  requires N, 16.9%).

*Degradation of  $\beta$ -Dinitrodiphenic Acid to Dinitrodiphenyl.*—A mixture of  $\beta$ -dinitrodiphenic acid with fine dry sand was distilled under the conditions described by Schmidt and Kämpf (*loc. cit.*); the yellow solid distillate, in agreement with their observation, melted at 240—245° after being extracted with alcohol, but the extract, which would have contained any dinitrodiphenyl which had been distilled, left practically no residue on distillation. The following modified procedure was therefore employed. A finely ground mixture of the acid (1 g.) with Naturkupfer C (0.1 g.) (compare Sabatier and Mailhe, *Compt. rend.*, 1914, 159, 217) was distributed by stirring over sufficient glass wool to fill an Anschütz flask of 75 c.c. capacity. This flask was connected through a larger one to a filter-pump. When the mixture was very gradually heated in an oil-bath under a pressure of 30 mm., a reaction of explosive violence occurred at 285°. After the dense white vapours had subsided, both the distillate and the blackened residue were extracted with boiling alcohol. The extract was evaporated, diluted with water, and treated with cold dilute ammonia; a small solid residue was obtained. By solution in benzene of the product (0.45 g.) from eight such experiments, dark, insoluble matter was removed, and fairly homogeneous, transparent crystals closely resembling those of 2:4'-dinitrodiphenyl were obtained. After further purification by solution in light petroleum-benzene to remove a small quantity of less soluble, granular material, the product melted at 93°. A mixture with authentic 2:4'-dinitrodiphenyl melted at the same temperature, even after fusion and resolidification. A mixture with 2:2'-dinitrodiphenyl, m. p. 124°, shrank at 68—70°, was largely molten at 90°, but not completely so until 118°. After resolidification, the opaque mass commenced to clear at 90°, was almost all molten at 100—103°, and entirely liquid at 105°. The product was therefore 2:4'-dinitrodiphenyl.

For the preparation of the compound from diphenyl, light petroleum (b. p. 70—80°) was much more effective in the late stage of purification than the methyl alcohol recommended by Fittig (*Annalen*, 1862, 124, 276).

*Nitration of 2-Nitrophenanthraquinone.*—After 2-nitrophenanthraquinone (10 g.) had been boiled under reflux with nitric acid (135 c.c.; *d* 1.5) and sulphuric acid (17 c.c.) for 30 minutes, the mixture was poured into water. From the solution of the precipitate in glacial acetic acid (1200 c.c.), 2:7-dinitrophenanthraquinone (8.9 g.), m. p. 301°, was deposited, whilst 0.4 g., m. p. 280—290°,



and 0.1 g., m. p. 225–293°, were recovered on concentrating the liquors to 200 c.c. and 50 c.c., respectively.

*Hydrolysis of the "Hydrazides" of  $\beta$ - and 6:6'-Dinitrodiphenic Acids.*—The "hydrazide" of  $\beta$ -dinitrodiphenic acid was prepared from the chloride in the manner already described for the corresponding derivative of 6:6'-dinitrodiphenic acid (Kenner and Stubbings, *loc. cit.*). It separates from acetone–light petroleum in small, colourless prisms, m. p. 294–295° (decomp.) (Found: N, 16.7.  $C_{14}H_8O_6N_4$  requires N, 17.0%), and does not reduce Fehling's solution. Repeated but unsuccessful attempts were made to prepare a well-defined acetyl derivative of the "hydrazide" corresponding to that previously described as having been obtained from the "hydrazide" of 6:6'-dinitrodiphenic acid. The compound (0.25 g.) was heated with nitric acid (4 c.c.; *d* 1.5) for 75 minutes at 100°; the solution then deposited dinitrodiphenic acid, m. p. 300–301°, on dilution with water (15 c.c.).

The "hydrazide" of 6:6'-dinitrodiphenic acid was obtained in colourless prisms, m. p. 310° (decomp.), by crystallisation from acetone–light petroleum. The acid formed by hydrolysis with fuming nitric acid at 100° for 40 minutes was isolated by evaporation of the liquors at the ordinary temperature in an exhausted desiccator over sodium hydroxide. Its melting point, 249–253°, was not depressed when the acid was mixed with 6:6'-dinitrodiphenic acid.

*Resolution of  $\beta$ -Dinitrodiphenic Acid into Optically Active Components.*—A solution of the acid (2 g.) and hydrated brucine (5.61 g.) in boiling water (1050 c.c.) deposited, on cooling, fern-shaped sprays of irregular plates (3.9 g.), m. p. 209° (decomp.). By successive concentration to 575 c.c., 200 c.c., and 50 c.c., further crops of 2.2 g., m. p. 206° (decomp.), 0.3 g., m. p. 209° (decomp.), and 0.4 g., m. p. 207° (decomp.), were respectively obtained. The salt was hydrated [Found:  $H_2O$ , 4.2.  $C_{60}H_{60}O_{16}N_6 \cdot 2\frac{1}{2}H_2O$  requires  $H_2O$ , 3.9%. Found, for the salt dried at 130°: N, 7.8.  $C_{12}H_6(NO_2)_2(CO_2H)_2 \cdot 2C_{23}H_{26}O_4N_2$  requires N, 7.5%]. For 1.5% solutions in 10*N*-acetic acid of the anhydrous salt from each of the first two fractions,  $[\alpha]_D = -13.29^\circ$  and  $-13.31^\circ$ , respectively. It was therefore not surprising that a solution of the sodium salt of the acid prepared from the brucine salt was inactive.

But when boiling solutions of the acid (4 g.) in alcohol (100 c.c.) and of quinine hydrate (9.2 g.) in alcohol (80 c.c.) were mixed, colourless, rectangular plates (5.7 g.), m. p. 178–179° (decomp.), separated on cooling; no further crystallisation occurred on concentration. On evaporating the alcohol, an oil remained, which was obtained in a solid condition by precipitation with light

petroleum from its solution in benzene. The melting point of the plates was unchanged after recrystallisation (Found:  $\text{C}_2\text{H}_6\text{O}$ , 2.45.  $\text{C}_{54}\text{H}_{56}\text{O}_{12}\text{N}_6 \cdot \frac{1}{2}\text{C}_2\text{H}_6\text{O}$  requires  $\text{C}_2\text{H}_6\text{O}$ , 2.4. Found, for the salt dried at  $130^\circ$ : N, 8.6.  $\text{C}_{54}\text{H}_{56}\text{O}_{12}\text{N}_6$  requires N, 8.6%). For a 1.43% solution of the dried salt in chloroform,  $[\alpha]_D^{25} = -218.1^\circ$ .

The more soluble salt melted at first at about  $93^\circ$ , but at  $162$ – $163^\circ$  after being heated to constant weight at  $120^\circ$  (Found: N, 8.55.  $\text{C}_{54}\text{H}_{56}\text{O}_{12}\text{N}_6$  requires N, 8.6%). For a 1.44% solution of the dried salt in chloroform,  $[\alpha]_D^{25} = -62.10^\circ$ .

d- $\beta$ -Dinitrodiphenic acid, obtained from the less soluble quinine salt by treatment with hydrochloric acid, melted at  $296^\circ$ , whilst a mixture of the acid with the racemic acid melted over the range  $285$ – $293^\circ$ .

For a 0.96% solution of the acid in ether,  $[\alpha]_D^{25} = +26.90^\circ$ , whilst for a 0.66% solution of the sodium salt in water,  $[\alpha]_D^{25} = -186.4^\circ$ .

l- $\beta$ -Dinitrodiphenic acid, obtained from the more soluble quinine salt, also melted at  $296^\circ$ . For a 0.92% solution of the acid in ether,  $[\alpha]_D^{25} = -26.46^\circ$ , and for a 1.29% solution of the sodium salt in water,  $[\alpha]_D^{25} = +179.4^\circ$ .

Two of the authors (G. H. C. and A. H.) take this opportunity of expressing their gratitude to the Department of Scientific and Industrial Research for grants which enabled them to take part in this work. The authors are indebted to the Research Fund Committee of the Chemical Society for a grant towards the purchase of materials.

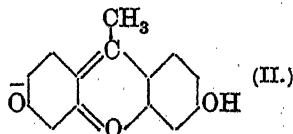
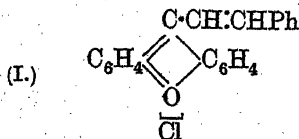
THE UNIVERSITY, SHEFFIELD.

[Received, December 28th, 1925.]

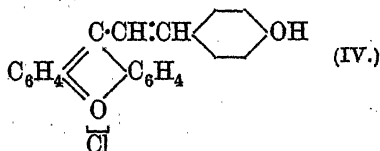
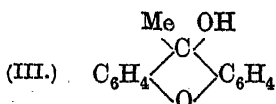
#### XCIV.—Styrylpyrylium Salts. Part VI. Styryl Derivatives of 9-Methylxanthylum Chloride and 3:6-Dihydroxy-9-methylxanthylum Chloride.

By HAROLD ATKINSON and ISIDOR MORRIS HEILBRON.

THE only styrylxanthylum salt recorded in the literature is 9-styrylxanthylum chloride (I), which Ziegler and Ochs (*Ber.*, 1922, 55, 2257) obtained by the action of  $\beta$ -bromostyrene and



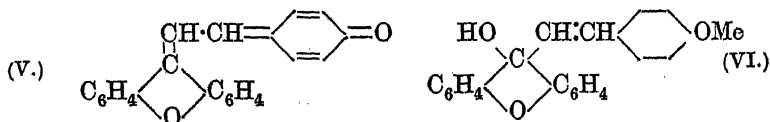
magnesium upon xanthone. A more detailed study of styryl-xanthylum salts has now been made in order to compare them with the members of the styrylbenzopyrylium series. As the method employed by Ziegler and Ochs could not readily be adopted for the preparation of salts containing substituents in either the styryl or the xanthylum residue, other methods of preparation had to be sought. The ease with which the anhydro-base, 6-hydroxy-9-methylfluorone (II), reacts with nitrous acid to form the *iso*-nitroso-derivative (Kehrmann, *Annalen*, 1910, **372**, 287) rendered it probable that a methyl group in position 9 in a xanthylum nucleus would show the same reactivity as an  $\alpha$ - or  $\gamma$ -methyl group does in the benzopyrylium series. In order to test this point, an attempt was made to prepare 9-methylxanthylum chloride which had previously been prepared by Decker (*Ber.*, 1905, **38**, 2493) in the form of its double ferrichloride salt by the action of magnesium methyl iodide upon xanthone. The free chloride can actually be isolated, but it is difficult to obtain in good yield. On the other hand, an ethereal solution of the easily accessible 9-methylxanthenol (III) may be utilised in place of the chloride itself. Thus, on saturation of the solution mixed with benzaldehyde with dry hydrogen chloride, 9-styrylxanthylum chloride, identical in all respects with the compound prepared by Ziegler and Ochs (*loc. cit.*), was readily obtained. Similar condensations have been



effected with *p*-hydroxybenzaldehyde, *p*-methoxybenzaldehyde, piperonal, and vanillin, and in all cases excellent yields obtained.

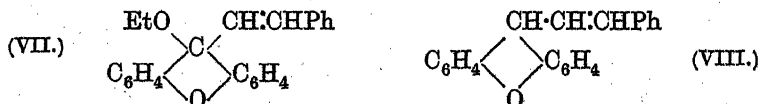
The styrylxanthylum salts containing substituents in the styryl residue are highly coloured, crystalline compounds, readily soluble in formic acid, giving deep red to purple solutions. In their reaction towards water and alkali, they behave similarly to the unsubstituted 2-styrylbenzopyryliums (Buck and Heilbron, *J.*, 1922, **121**, 1198). Thus, when 4'-hydroxy-9-styrylxanthylum chloride (IV) was dissolved in dilute formic acid, a reddish-violet solution resulted which on dilution with a large excess of water slowly changed to blue. This colour effect we attribute, as in former cases, to formation of the quinonoid anhydro-base (V), for with 4'-methoxy-9-styrylxanthylum chloride, where such isomerisation is precluded, the solution rapidly becomes opalescent and decolorised, followed by deposition of the colourless carbinol base (VI).

3' : 4'-Methylenedioxy-9-styrylxanthylum chloride, which dissolves in formic acid with a blue colour, reacts similarly. The same effect



is noted on treatment of the formic acid solutions with dilute sodium hydroxide. On the other hand, with the 4'-hydroxy-derivatives the quinonoid anhydro-bases are first precipitated and then slowly isomerise to the colourless carbinol bases (compare Dilthey and Taucher, *Ber.*, 1920, **53**, 252). In all cases, the effect of heat on the colourless carbinol solutions produces a reversion in colour, a fact indicating that at higher temperatures the oxonium bases are more stable than the isomeric carbinol compounds. This phenomenon has also been observed by Bunzly and Decker (*Ber.*, 1904, **37**, 2931) in the case of 9-phenylxanthanol.

The behaviour of these styrylxanthylum chlorides towards alcohol is peculiar. Ziegler and Ochs (*loc. cit.*) noted that on trituration of 9-styrylxanthylum chloride with alcohol, 9-styrylxanthyl ethyl ether (VII) was formed, while, on the other hand, boiling with this solvent produced 9-styrylxanthen (VIII). A

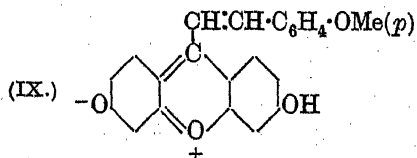


preliminary study of the styrylxanthylum chlorides containing substituents in the styryl residue has shown that when these are kept in contact with small quantities of alcohol, they are gradually converted into colourless substances, all of which crystallise from acetone in well-defined crystals with sharp melting point. The compounds thus prepared have been analysed, but in each case the carbon content is too high for formulation either as an ethyl ether, xanthen or allene derivative. The formation of the last type of compound from other styryl derivatives was noted by Meyer and Schuster (*Ber.*, 1922, **55**, 815), and Ziegler and Ochs, by boiling 9-styrylxanthenol with glacial acetic acid, obtained a compound the composition of which would agree with that of an allene derivative. A full investigation of these interesting compounds is at present being undertaken.

Walker and Heilbron (*J.*, 1925, **127**, 685) have shown that in the  $\gamma$ -styrylbenzopyryliums the presence of a free hydroxyl group in the meta-position to pyrylium oxygen inhibits the change to quinonoid anhydro-base on water dilution. In order to ascertain

whether a similar effect holds in this series, styrylxanthylum salts prepared from 3:6-dihydroxy-9-methylxanthylum chloride have been examined. The latter compound, which has been described by Kehrmann (*loc. cit.*), can be isolated directly in good yield by continuously passing dry hydrogen chloride into a molten mixture of resacetophenone and resorcinol until the mass solidifies.

**3:6-Dihydroxy-9-styrylxanthylum Salts.**—The general method employed was to saturate with dry hydrogen chloride a suspension of 3:6-dihydroxy-9-methylxanthylum chloride in alcohol containing a slight excess of the required aldehyde. Condensation usually started in the cold and was completed by boiling under reflux; the suspended chloride then gradually disappeared and the condensation product separated either from the boiling solution or on cooling. These salts differ from those having the unsubstituted xanthylum nucleus in being soluble in alcohol without change, whilst the colour of the solutions both in this solvent and in formic acid is considerably lighter. A notable point is that whereas 3:6-dihydroxy-9-methylxanthylum chloride is characterised by its strong fluorescence in alkaline solution, substitution of the styryl radical for the methyl group caused the complete disappearance of this property. The colour changes observed on dilution with water or treatment with alkali differ essentially from those of the unsubstituted styrylxanthylum members. A neutral alcoholic solution of 3:4':6-trihydroxy-9-styrylxanthylum chloride remains unaltered on dilution, and in presence of alkali the orange-red colour only changes to bright red, due doubtless to salt formation. 3:6-Dihydroxy-4'-methoxy-9-styrylxanthylum chloride reacts similarly, for neither on dilution nor in presence of alkali does isomerisation to the carbinol base occur. The non-formation of this can only be attributed to the presence of the hydroxyl groups, which stabilise the molecule, presumably by formation of the betaine (IX). The same phenomenon must consequently hold for the 4'-hydroxy-analogue, but apart from this no structural change from benzenoid to quinonoid can be assumed.



#### EXPERIMENTAL.

**9-Methylxanthylum chloride** was prepared by a modification of Decker's method (*loc. cit.*). Xanthen (30 g.) was dissolved in

boiling benzene (250 c.c.), and the Grignard reagent (12 g. of magnesium and 66 g. of methyl iodide) gradually added. The solution immediately became orange and a yellow solid separated. This was rapidly reabsorbed, however, and later a colourless, crystalline compound separated from the greyish-green liquid. The whole was boiled under reflux for 1 hour, after which the ether and about half the benzene were removed. The solid was filtered off from the cold solution, washed with dry ether, and decomposed with cold water. The yellow solution so formed was repeatedly extracted with ether until the aqueous layer gave only a pale yellow colour on the addition of concentrated hydrochloric acid. After drying over sodium sulphate, this ethereal solution was employed directly for the preparation of the styryl salts. In order to obtain 9-methylxanthylum chloride, the solution was saturated with dry hydrogen chloride; the colour then changed from pale yellow to green and on standing in the ice-chest, dark red crystals separated. After recrystallisation from a mixture of anhydrous formic acid and ether containing hydrogen chloride, the salt was obtained in golden needles, m. p. 175°, and identified by means of the double ferrichloride, m. p. 204°, and mercurichloride (compare Decker, *loc. cit.*). The melting point of the ferrichloride is given in the literature as 240°, but this is possibly a typographical error.

*9-Styrylxanthylum Chlorides.*—The general method of preparation of these salts consisted in the addition of the aldehyde in slight excess to the dry ethereal solution of 9-methylxanthanol, the mixture being then saturated with dry hydrogen chloride, when condensation readily took place. The actual amount of xanthanol in solution was not ascertained, but the Grignard reaction, by means of which it was prepared, was assumed to have given a quantitative yield.

*9-Styrylxanthylum chloride* rapidly separated from the condensation mixture of 9-methylxanthanol and benzaldehyde either as golden, glistening plates or as red needles with a bright green sheen. The plates melted at 95°, the same melting point as that given by Ziegler and Ochs (*loc. cit.*), but the red needles melted over a range of temperature (66–92°) and probably contained some easily lost addenda. This salt was proved to be identical with that prepared by Ziegler and Ochs by means of the deep red double salt with zinc chloride (m. p. 188°) and its ethyl ether (m. p. 168–169°).

*4'-Hydroxy-9-styrylxanthylum chloride.* On passing dry hydrogen chloride into the well-dried ethereal solution of 9-methylxanthanol and excess of *p*-hydroxybenzaldehyde, the solution gradually passed

through orange to dark red and a violet oil with bronze reflex separated. The mixture having been left in the ice-chest for several hours, the ether was poured off; the oil gradually solidified to a green, amorphous mass. This was taken up in a small amount of warm anhydrous formic acid previously saturated with hydrogen chloride, and dry ether was added to the cold filtered solution in small quantities at a time; the styryl salt then separated in long, bright-green, lustrous needles containing 1 mol.  $\text{HCO}_2\text{H}$ . These were immediately transferred to a large test-tube, which was then evacuated, whereby adherent hydrogen chloride was removed and the crystals were rendered stable. If this was not done, the compound tended to become resinous, a tendency exhibited by all members of this series. The salt was readily soluble in cold formic acid and in hot glacial acetic acid, giving dark violet solutions. It was sparingly soluble in cold chloroform to a blue solution which changed to reddish-brown on warming but reverted to blue on cooling. The same colour change on heating was shown by a solution in nitrobenzene. When a large volume of water was added to a very dilute formic acid solution (wine-red colour), no immediate change of colour occurred, but on standing (6 hours) the solution became pure blue. The addition of water to a more concentrated formic acid solution caused the immediate separation of a violet, amorphous precipitate, presumably the anhydro-base (V) (Found: C, 69.4; H, 4.5; Cl, 9.4.  $\text{C}_{22}\text{H}_{17}\text{O}_4\text{Cl}\cdot\text{HCO}_2\text{H}$  requires C, 69.4; H, 4.5; Cl, 9.3%). In contact with absolute alcohol, the salt was partly converted into a colourless, crystalline substance, but this change was not absolutely complete despite repeated trituration, even after 15 days. The substance crystallises from acetone in long, colourless needles, m. p.  $228^\circ$  (Found: C, 85.0; H, 5.8%).

*4'-Methoxy-9-styrylxanthylum chloride* separated from the condensation liquor in dark green crystals. Considerable difficulty was experienced in obtaining it in a stable crystalline state sufficiently pure for analysis, but this was ultimately accomplished by crystallisation from chloroform containing hydrogen chloride; it then separated in bright green needles, m. p.  $98^\circ$ , which were rendered stable by removal of all addenda in a vacuum. The salt dissolved readily in formic and glacial acetic acids, giving dark violet solutions. When a dilute solution in formic acid was treated with water, a strong opalescence immediately developed, the wine-red colour rapidly faded, and the colourless carbinol base was deposited. As with the 4'-hydroxystyryl salt, long trituration with alcohol gave a colourless compound, m. p.  $194^\circ$ , of undetermined constitution. The *ferrichloride*, prepared by the action of powdered hydrated ferric

chloride on a solution of 4'-methoxy-9-styrylxanthylum chloride in formic acid, separated from glacial acetic acid in long, copper-coloured plates which softened and turned blue at 175° and decomposed with inflation at 212° (Found : C, 51.5; H, 3.2; Cl, 27.7; Fe, 10.5.  $C_{22}H_{17}O_2Cl_4Fe$  requires C, 51.7; H, 3.3; Cl, 27.8; Fe, 10.9%).

4'-Hydroxy-3'-methoxy-9-styrylxanthylum chloride crystallised from formic acid in golden-brown needles which contained a molecule of formic acid (m. p. 135°). The salt was readily soluble in cold formic acid and in hot glacial acetic acid, giving royal-blue solutions. Neutralisation of a dilute formic acid solution with sodium carbonate precipitated the colour base, which was gradually converted into the colourless carbinol base (Found : C, 67.1; H, 4.6; Cl, 8.9.  $C_{22}H_{17}O_3Cl.HCO_2H$  requires C, 67.2; H, 4.6; Cl, 8.7%).

3' : 4'-Methylenedioxy-9-styrylxanthylum chloride could not be obtained pure, for although it separated from the condensation mixture in green crystals, attempts to recrystallise these from either formic acid or glacial acetic acid with or without the addition of hydrogen chloride resulted in the formation of a yellow oil, which gradually solidified to a colourless compound. Recourse was made, therefore, to analysis of the zinc chloride double salt, which was readily prepared by suspending the crude xanthylum chloride in cold formic acid and shaking vigorously with zinc chloride in hydrochloric acid. The salt separated from glacial acetic acid in glistening, green needles (Found : C, 49.6; H, 3.1; Cl, 20.3.  $C_{22}H_{15}O_3Cl_3Zn.H_2O$  requires C, 51.2; H, 3.3; Cl, 20.6%).

3 : 6-Dihydroxy-9-methylxanthylum Chloride.—Dry hydrogen chloride was passed into a molten mixture of resacetophenone (10 g.) and resorcinol (7.2 g.) (oil-bath at 140—150°). The melt gradually turned red and, after several hours, became semi-solid. The stream of hydrogen chloride was continued until the mass became too viscous, the temperature being gradually raised to 170°. The solid mass was dissolved in boiling anhydrous formic acid (80 c.c.); the xanthylum chloride then separated in reddish-yellow needles with a characteristic blue metallic reflex. On several occasions, however, the salt was deposited as a chocolate powder, which was again recrystallised from formic acid containing hydrogen chloride. It is soluble in alcohol, acetone, or formic acid and insoluble in ether or benzene. It dissolves in sodium hydroxide solution to a reddish-brown solution which when dilute shows an intense green fluorescence. With sodium acetate it yields the base in the form of brick-red flocks.

3 : 4' : 6-Trihydroxy-9-styrylxanthylum Chloride.—The parent



chloride (5 g.) was suspended in 70 c.c. of alcohol together with *p*-hydroxybenzaldehyde (2.6 g.), and dry hydrogen chloride was passed into the cold solution; the xanthylum chloride then gradually dissolved. After  $\frac{1}{2}$  hour the styrylxanthylum chloride (4.3 g.) separated from the deep red solution as a red, amorphous solid. On recrystallisation from anhydrous formic acid containing hydrogen chloride, it formed long needles which appeared red by transmitted and green by reflected light. On heating the chloride changed to red and melted with inflation at 273–274°. It is readily soluble in hot formic acid, sparingly soluble in alcohol or acetone to orange-red solutions, whilst in dilute sodium hydroxide it dissolves, giving a permanent bright claret-red solution (Found: C, 65.1; H, 4.2; Cl, 9.0.  $C_{21}H_{15}O_4Cl \cdot H_2O$  requires C, 65.5; H, 4.4; Cl, 9.2%).

3 : 6-Dihydroxy-4'-methoxy-9-styrylxanthylum chloride separated as a dark red, amorphous solid (70% yield) on passing hydrogen chloride into a boiling alcoholic suspension of equimolecular quantities of the parent chloride and anisaldehyde. It was purified by boiling with alcohol, which removed any uncondensed products, and was then crystallised from formic acid containing hydrogen chloride. It forms golden-coloured plates with a metallic sheen which on heating change to green and melt at 282° (decomp.). It is very sparingly soluble in boiling alcohol or acetone, but readily soluble in hot formic acid. It dissolves in warm dilute sodium carbonate to a bright red solution, from which the base separates on cooling (Found: C, 65.9; H, 4.6; Cl, 8.7.  $C_{22}H_{17}O_4Cl \cdot H_2O$  requires C, 66.2; H, 4.8; Cl, 8.9%).

3 : 4' : 6-Trihydroxy-5'-methoxy-9-styrylxanthylum chloride crystallises from formic acid in reddish-violet needles which appear green by reflected light (m. p. 244–245°). It is readily soluble in alcohol, acetone, or hot formic acid and dissolves in dilute sodium hydroxide solution with a deep reddish-violet colour. It is extremely hygroscopic and specimens were dried at 100° immediately prior to analysis (Found: C, 66.6; H, 4.4; Cl, 8.8.  $C_{22}H_{17}O_5Cl$  requires C, 66.6; H, 4.3; Cl, 8.9%).

3 : 6-Dihydroxy-4' : 5'-methylenedioxy-9-styrylxanthylum chloride separates from formic acid containing hydrogen chloride in bronze-coloured needles which, on heating, turn green and decompose at 316°. It is very sparingly soluble in alcohol, but dissolves readily in boiling formic acid to a red solution (Found, in material heated at 80° for several hours: C, 66.8; H, 3.9; Cl, 9.3.  $C_{22}H_{15}O_5Cl$  requires C, 66.9; H, 3.8; Cl, 9.0%).

3 : 6-Dihydroxy-4'-dimethylamino-9-styrylxanthylum Chloride.—A suspension of the parent chloride (5 g.) and *p*-dimethylamino-

benzaldehyde (3.2 g.) in 100 c.c. of alcohol was boiled for 10 minutes under reflux without addition of hydrogen chloride, the condensation product separating as a hard, green solid. On recrystallisation from a large volume of alcohol, it formed microscopic, green needles which on heating changed to red. It is sparingly soluble in alcohol or acetone, giving intense green solutions which change to claret-red on dilution with water. Addition of hydrochloric acid to the alcoholic solution produces a yellow solution of the xanthylum chloride hydrochloride. The salt dissolves in aqueous sodium hydroxide to a bright scarlet solution, which is not altered on further dilution (Found: C, 66.6; H, 5.2; Cl, 8.8.  $C_{23}H_{20}O_3NCl \cdot H_2O$  requires C, 67.1; H, 5.3; Cl, 8.6%).

We wish to record our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (H. A.) which enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL.

[Received, December 28th, 1925.]

### XCV.—*Arylsulphuric Acids.*

By GEORGE NORMAN BURKHARDT and ARTHUR LAPWORTH.

THE use of dialkylanilines in place of pyridine for the preparation of arylsulphuric acids by Verley's method [*Bull. Soc. chim.*, 1901, 25, 46; compare Durand and Huguenin, Brit. Pat. 186057 (1922), 202630 and 202632 (1923)] has been found to lead to rather better yields and recovery of tertiary base is simplified.

Diethylaniline (100 g.;  $2\frac{1}{2}$  mols.) or the equivalent quantity of dimethylaniline in carbon disulphide (100 c.c.) was stirred mechanically and cooled to  $-10^\circ$ . Chlorosulphonic acid (34 g.; 1.1 mols.) was run in steadily during 15 minutes, the temperature being maintained below  $10^\circ$ . Phenol (25 g.; 1 mol.) in carbon disulphide (50 c.c.) was then added all at once, the mixture stirred for an hour, and the disulphide thereafter removed by distillation on a steam-bath. The cold, viscous residue was run into a solution of sodium hydroxide (22 g.) in water (150 c.c.) containing 10 g. of hydrated barium hydroxide,\* with vigorous shaking, the temperature being kept below  $35^\circ$ . A large proportion of the diethylaniline could

\* For certain purposes, the use of excess of ammonia instead of the hydroxide of an alkali metal is advantageous; but in this case, before removing the tertiary base in a current of steam, it is necessary to add sufficient barium hydroxide to convert all salts present into barium salts, as ammonium phenyl sulphate may suffer hydrolysis in the steam distillation process.

then be separated directly and the remainder removed by steam distillation or by extraction with benzene; the aqueous residue on direct evaporation yielded 90% of the theoretical quantity of sodium phenyl sulphate together with 7% of sodium chloride.

If the base and phenol were mixed before the chlorosulphonic acid was added, the yields never exceeded 60% of the theoretical.

*Use of Sulphuric Anhydride in place of Chlorosulphonic Acid.*—The authors carried out a number of experiments on the use of sulphuric anhydride in place of the chlorosulphonic acid employed by Verley (*loc. cit.*), as the formation of hydrogen chloride in the preparation is often disadvantageous. The experiments were completed before the patents of Durand and Huguenin (Brit. Pat. 202632 of 1923) came to their notice, but some of the observations made were not redundant and appear worthy of record.

As it was evident that the use of sulphuric anhydride as sulphating agent for phenols would render it easy to isolate pure products, trials of a number of organic media as solvents were made. The liquids were cooled and the anhydride was distilled slowly into them. Chloroform and carbon tetrachloride were decomposed rapidly, yielding carbonyl chloride even with most careful cooling, and carbon disulphide evolved carbonyl sulphide. Diethylaniline could not be made to dissolve the anhydride without charring and sulphonation; hexane did not appear to dissolve the anhydride as such, but was rapidly attacked when in contact with it: the nature of the reaction in the latter instance is under investigation. Experiments in which sulphuric anhydride was distilled into a cooled solution containing both phenol and diethylaniline in carbon tetrachloride gave more promising results, but even in presence of the tertiary base about 13% of the anhydride was destroyed by reaction with the tetrachloride, and the mixed salts obtained at the end of the operation contained 8% of inorganic chloride.

The only solvent found to dissolve sulphuric anhydride readily and without decomposition was liquid sulphur dioxide, and the following is an account of one of the experiments in which it was tried as solvent for sulphating phenols.

A solution of sulphuric anhydride (19 g.) in 80 c.c. of liquid sulphur dioxide was slowly added with vigorous stirring to phenol (20 g.) and diethylaniline (60 g.) in a wide-mouthed flask, cooled in a freezing mixture. After remaining over-night to allow most of the solvent to evaporate, it was found that much of the latter was obstinately retained and had to be removed by heating for an hour on a steam-bath. The product, after cooling, was neutralised with aqueous sodium hydroxide and sufficient barium hydroxide to precipitate inorganic sulphate. Nearly pure sodium phenyl

sulphate in 60% yield was isolated on removal of diethylaniline and evaporation of the aqueous residue.

*Use of Pyridine Sulphuro-anhydride in the Preparation of Salts of Phenylsulphuric Acids.* [With FRANK ASHWORTH].—This method is virtually a modification of the process last described, inasmuch as sulphuric anhydride with a tertiary base, in this instance pyridine, is used. The following is an example of its application to a nitrophenol.

Sulphur trioxide (25 g.) is slowly distilled, with stirring and drastic cooling, into pyridine (29 g.; 1.75 mols.). Benzene (200 c.c.) is now added, and the whole heated to boiling\* under a reflux condenser. *p*-Nitrophenol (30 g.; 1 mol.) is next introduced and the whole boiled for 4 hours, during which time the pyridine salt of *p*-nitrophenylsulphuric acid crystallises out. The mixture is cooled, poured into a slight excess of aqueous potassium hydroxide, the benzene distilled off under diminished pressure, the residual solution made just acid with acetic acid, and unchanged nitrophenol (2 g.) extracted with ether. The solution is rendered slightly alkaline once more and the water and pyridine evaporated off under diminished pressure, when potassium *p*-nitrophenyl sulphate is obtained in yields of 90—94% of the theoretical.

Eugenol under similar conditions gave a 70% yield of potassium eugenyl sulphate.

*o*-Nitrophenol proved much more difficult to attack than the para-isomeride. Yields of the sulphate up to 25% were obtained when equivalent proportions of *o*-nitrophenol and pyridine sulphuro-anhydride were used, and 56% yields with twice the theoretical amount of the latter.

*Use of Pyrosulphate and Tertiary Bases in the Preparation of Phenylsulphuric Acids.*—It is somewhat remarkable that there are no published records of attempts to extend or improve upon the results obtained by Baumann (*Ber.*, 1878, **11**, 1907), who succeeded in making potassium phenyl sulphate from phenol by means of potassium pyrosulphate. He worked with aqueous solutions only, however, with potassium hydroxide as condensing agent, and the yields were very poor. The present authors have found that good yields of the phenyl sulphates can be obtained by heating finely powdered potassium pyrosulphate with a solution of the phenol or naphthol in dry dimethylaniline, followed by extraction of the product with aqueous alkali.

A mixture of phenol (1 mol.) and dimethyl- or diethyl-aniline (1 mol.) was heated on a steam-bath and stirred mechanically while

\* Control experiments showed that pyridine sulphuro-anhydride has no appreciable action on boiling benzene.

finely powdered potassium pyrosulphate\* ( $1\frac{1}{2}$  mols.) was added; the suspension was stirred and heated for 8 hours. The reaction mixture was poured into a suspension of excess of baryta in cold water, the base being subsequently removed by steam distillation, the excess of baryta being precipitated by means of carbon dioxide. After filtering and evaporating, potassium phenyl sulphate in 80–85% yield was easily isolated.

Another experiment using phenol (1 mol.), base (3 mols.), and pyrosulphate ( $2\frac{1}{2}$  mols.), heated and stirred for 4 hours, gave a yield of 90%.

The method was also found satisfactory for  $\alpha$ - and  $\beta$ -naphthols, and for eugenol and isoeugenol, except that in all these cases it was impossible to use barium hydroxide on account of the low solubility of the salts of the products. A slight excess of potassium hydroxide was therefore added and the base separated while the solution was hot.

*Notes on the Properties of the Salts of Arylsulphuric Acids.*—Baumann and Verley (*loc. cit.*) recorded (a) that the potassium salts of the arylsulphuric acids are stable to alkalis, but are readily hydrolysed by acids; (b) that they decompose, with some isomerisation to sulphonates, at 150–200°; (c) one or two physical properties in a few instances. Heymann and Koenigs oxidised potassium *o*- and *p*-tolyl sulphates to the corresponding carboxylic acids (*Ber.*, 1886, 19, 704). In the present investigation many of the above observations were confirmed and extended, and a variety of salts of arylsulphuric acids examined in some detail.

The salts show some variations in their ease of hydrolysis. The alkali salts are stable at 100° in neutral aqueous solution and require heating to boiling before rapid hydrolysis sets in in presence of mineral acid. The barium salt is decomposed on heating to 100° in aqueous solution for  $1\frac{1}{2}$  hours, after which the hydrolysis proceeds rapidly to completion in 2 hours. The ammonium and magnesium salts are of intermediate stability. All the salts are stable at 100° in an aqueous solution of sodium acetate even in presence of a considerable concentration of acetic acid. Hydrolysis of the potassium salt is also brought about by heating at 150° with strong alkali or with half-concentrated ammonia at 190–220° for 4 hours. In the latter case, no aniline is produced.

\* Potassium pyrosulphate was made by heating powdered potassium hydrogen sulphate, under 2–3 mm. pressure, in a bolt-head flask on a sand-bath. The reaction proceeded at 270–330° and was stopped when the temperature began to rise rapidly. The mass was then poured on to an iron plate and allowed to cool in a desiccator; it contained 90% of pyrosulphate. The salt was powdered and sieved as rapidly as possible immediately before application in the above reactions, otherwise it deteriorated.

Heating with aniline gave no indication of replacement of the hydroxyl group. Diazo-compounds do not couple to an appreciable extent with salts of phenylsulphuric acid in alkaline solution, and nitrous acid is without action, even after several days. Concentrated nitric acid rapidly decomposes the alkali salts, producing a mixture of nitro-derivatives without tarring or much evolution of heat. The bromination of salts of phenylsulphuric acids is described in another communication. Potassium phenyl sulphate crystallises in anhydrous, rhombohedral or six-sided plates with apex angle  $95^\circ$ . It dissolves to the extent of 0.7% in alcohol and 14% in water at  $17^\circ$ , and is freely soluble in both media when hot (Found: K, 18.3. Calc. for  $C_6H_5O_4SK$ , K, 18.5%).

The sodium salt forms rhombic plates consisting of aggregates of twinned leaflets. It dissolves to the extent of 7% in alcohol and 31% in water at  $17^\circ$ , and is freely soluble in both media when hot (Found: Na, 9.3. Calc. for  $C_6H_5O_4SN_{a,3}H_2O$ , Na, 9.2%). The barium salt forms fine granules and is rather less readily soluble in water than is barium chloride; in hot or cold alcohol, it dissolves to the extent of about 15%; when the moist salt is exposed in a steam-oven it is quantitatively decomposed in a few minutes, phenol being liberated, and the same change occurs at the ordinary temperature in the course of a few days. The ammonium salt is extremely soluble in cold water and crystallises in hydrated, rhombohedra composed of thin plates like the sodium salt. The magnesium salt forms small, nacreous, rectangular or six-sided plates; it is less soluble in cold water than any of the other salts examined.

Salts of the isomeric tolylsulphuric acids are very sparingly soluble in cold alcohol and acetone and only slightly soluble in hot; they can be recrystallised from 85% alcohol, and, in the case of the *p*-tolyl derivative, from acetone containing 2% of water. They are very freely soluble in acetone containing 5% of water. The *o*-salt is soluble to the extent of 22% in water at  $17^\circ$ , the *m*- 9%, and the *p*- 10%.

*p*-Toluidine tolyl sulphates are characteristic. They were prepared as follows: Potassium tolyl sulphate (5.5 g.) was added to a hot solution of *p*-toluidine (2 g.) in 50 c.c. of alcohol, the mixture stirred for a minute with the liquid just below the boiling point, and *p*-toluidine hydrochloride (3.5 g.) added. The solution was boiled and shaken for a few minutes, and the potassium chloride (1.8 g.) which separated was filtered off. On evaporation, the liquor gave an almost theoretical yield of the toluidine tolyl sulphate, which was washed with benzene and recrystallised from benzene containing 5% of alcohol. The salts from *o*- and *p*-cresols are fairly soluble in

water and readily in alcohol and acetone but insoluble in benzene. On recrystallisation, they formed matted, woolly needles which on melting or heating for some time at  $110^{\circ}$  gave *p*-toluidine sulphate and free cresol. The salt from *o*-cresol melted sharply with decomposition at  $125\text{--}127^{\circ}$ , and the *p*-salt at  $149\text{--}151^{\circ}$ .

*Potassium m-carboxyphenyl sulphate* was prepared by oxidation of the *m*-tolylsulphate. The latter (30 g.) was dissolved in water (100 c.c.) containing a little potassium hydroxide. A hot saturated solution of potassium permanganate (60 g.) was added to the solution, and the mixture heated on the steam-bath for 8 hours, after which the excess permanganate was reduced by means of alcohol, and the precipitate removed by filtration. The filtrate after cooling was rendered slightly acid with hydrochloric acid. The flocculent precipitate formed was collected, washed, and recrystallised from 70% alcohol. The yield was 80%. The salt forms plates: 3.2 parts dissolve in 100 parts of water at  $17^{\circ}$ ; it is readily soluble in acetone containing 10% of water (Found: K, 15.3.  $\text{C}_7\text{H}_5\text{O}_6\text{SK}$  requires K, 15.3%). It gave no coloration with ferric chloride. It was hydrolysed, on boiling with mineral acid, yielding *m*-hydroxybenzoic acid and potassium hydrogen sulphate.

*Salts of Naphthylsulphuric Acids.*—These are readily obtained in yields of 80–90% by the methods described on pp. 684 and 686. High purity of the naphthols is important in using the latter method or the products are discoloured.

*Potassium  $\alpha$ -naphthyl sulphate* crystallises from water as a coarse, crystalline powder or in long, soft needles. It dissolves in 40 parts of water at  $17^{\circ}$ , is freely soluble in hot water, and almost insoluble in most of the usual organic media (Found: K, 14.7.  $\text{C}_{10}\text{H}_7\text{O}_4\text{SK}$  requires K, 14.9%).

*Potassium  $\beta$ -naphthyl sulphate* resembles its isomeride in general appearance and characters, but its crystals are hydrated. It dissolves in 70 parts of water at  $17^{\circ}$  (Found: K, 11.9.  $\text{C}_{10}\text{H}_7\text{O}_4\text{SK} \cdot 4\text{H}_2\text{O}$  requires K, 11.7%).

Both these salts are stable to boiling alkalis and to boiling dilute acetic acid in presence of sodium acetate; they are easily hydrolysed, however, by hot dilute mineral acids. They are at once attacked in aqueous solution by bromine, and precipitates soluble in ether are formed together with free sulphuric acid; the elimination of the sulphate residue is not, however, complete after several minutes in presence of excess of bromine.

A considerable amount of time was spent in investigating the oxidation of the isomeric potassium naphthyl sulphates with alkaline permanganate in aqueous solution. It was found that rapid oxidation took place at  $80^{\circ}$ , and from the quantity of free

inorganic sulphate formed, that about 42% of the  $\alpha$ -salt underwent oxidation in the unsubstituted ring, and in the case of the  $\beta$ -isomeric about 62%. Numerous attempts to separate from the resulting mixtures the sulphates of the hydroxyphthalic, hydroxyphthalonic acids, or the corresponding products formed after elimination of the sulphate radicals were not successful, owing mainly to the excessive solubility of these acids and their derivatives.

From potassium  $\alpha$ -naphthyl sulphate, a small amount of the hydroxyphthalic acid (m. p. 150°) and some phthalic acid were obtained (compare Miller, *Annalen*, 1881, 208, 247).

The authors wish to acknowledge a grant from the Research Fund of the Chemical Society towards the expenses of this investigation, and a maintenance grant to one of them (G. N. B.) from the Department of Scientific and Industrial Research which enabled him to take part in the later sections of the work.

THE UNIVERSITY, MANCHESTER.

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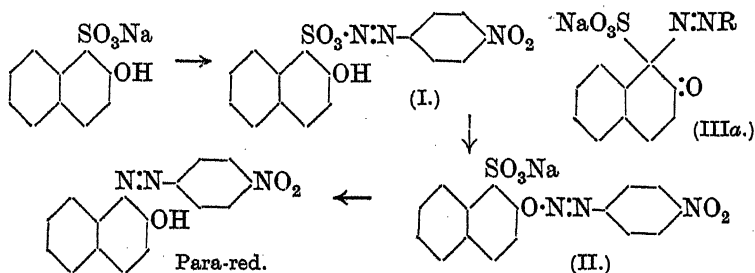
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XCVI.—*A New Reaction of Certain Diazosulphonates derived from  $\beta$ -Naphthol-1-sulphonic Acid. Part I. Preparation of Phthalazine, Phthalazone, and Phthalimidine Derivatives from 4'-Nitrobenzene-2-naphthol-1-diazosulphonate.*

By FREDERICK MAURICE ROWE, ESTHER LEVIN, ALAN CHAMLEY BURNS, JOHN STANLEY HERBERT DAVIES, and WOLFE TEPPER.

SOME  $\beta$ -naphtholsulphonic acids condense with diazo-compounds in acid solution to form stable diazosulphonates; thus,  $\beta$ -naphthol-1-sulphonic acid or oxy-Tobias acid (Bayer & Co., Brit. Pat. 11757 of 1895) gives diazosulphonates which Grant Hepburn (Brit. Pat. 116360) found to possess interesting properties. For example, Para-red is obtained in substance quantitatively by dissolving one molecular proportion of 4'-nitrobenzene-2-naphthol-1-diazosulphonate in an aqueous solution of sodium carbonate or of one molecular proportion of sodium hydroxide, and then acidifying the cold solution. Diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid appear to be the only examples in which the stabilising component can provide subsequently an azo-coupling component. Bucherer (*Ber.*, 1909, 42, 47; "*Lehrbuch der Farbenchemie*," 1914, 125), without giving experimental details, explains this reaction thus:





Wahl and Lantz (*Bull. Soc. chim.*, 1923, **33**, 97) have re-examined the above reaction and agree with Bucherer's conclusion that compound (II) is a diazo-oxide, but were unable to isolate an analogous compound from 1-bromo-(or chloro)- $\beta$ -naphthol, although the latter reacts with diazotised *p*-nitroaniline to form Para-red as shown by Hewitt and Mitchell (*J.*, 1906, **89**, 1169).

As Wahl and Lantz state that they propose to study the diazo-oxides which can be prepared from  $\beta$ -naphthol-1-sulphonic acid and other diazo-compounds, we must mention here that we began our present investigation in 1918 with an examination of these compounds. Diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid are stable, whereas the compounds formed from them by the action of one molecular proportion of alkali are unstable and particularly sensitive to acids. If the latter are diazo-oxides, it is not clear why they should be more reactive and unstable than diazosulphonates, and, in view of our other results, we suggest that they are sodium aryl-1-azo- $\beta$ -naphthaquinone-1-sulphonates of the general formula (IIIa). Compounds of this type would be hydrolysed readily by cold dilute acid, forming azo- $\beta$ -naphthol derivatives. It might be anticipated that such compounds would give different reduction products from those obtained from corresponding diazo-oxides, but they are so unstable that the reduction products more probably would be derived from the corresponding azo- $\beta$ -naphthol derivative, owing to the preliminary elimination of the sulphonic group. In support of this, we find that even the more stable diazosulphonates give 1-amino-2-naphthol on reduction.

Grant Hepburn (*loc. cit.*) observed that although Para-red is obtained by acidifying a solution of 4'-nitrobenzene-2-naphthol-1-diazosulphonate in one molecular proportion of aqueous sodium hydroxide, this is not the case if an excess of sodium hydroxide is used, and he handed over the investigation of this interesting reaction to one of us (F. M. R.).

When the orange solution of 4'-nitrobenzene-2-naphthol-1-diazosulphonate in aqueous sodium carbonate is added to an excess of cold aqueous sodium hydroxide, or vice versa, the temperature

risers and a crimson colour is developed immediately, which changes slowly to orange-brown, or more rapidly when warmed on the water-bath. There is no evolution of nitrogen, and no formation of sodium  $\beta$ -naphthol-1-sulphonate or sodium *p*-nitrophenylnitrosoamine. Subsequent acidification gives traces only of Para-red, and, consequently, a reaction has occurred in which the whole of the diazosulphonate has taken part. No organic by-products can be detected and a homogeneous yellow compound can now be isolated in excellent yield.

In order to test the generality of this reaction, various diazosulphonates were prepared, using other diazo-compounds in place of diazotised *p*-nitroaniline. Each diazosulphonate was converted by sodium carbonate into a sodium aryl-1-azo- $\beta$ -naphthaquinone-1-sulphonate, many of which were isolated in a well-crystalline condition, and all of which were converted quantitatively into the corresponding azo-derivative of  $\beta$ -naphthol, with elimination of the sulphonic group, by the action of cold dilute acid. On the other hand, only certain diazosulphonates give rise to the new reaction with sodium hydroxide. For example, the compounds from aniline, *o*- and *p*-toluidine, 2:5-dichloroaniline, tribromoaniline, sulphanilic acid, *p*-aminoacetanilide, anthranilic acid, *p*-aminobenzonitrile,  $\alpha$ - and  $\beta$ -naphthylamine, and benzidine are decomposed by sodium hydroxide with formation of sodium  $\beta$ -naphthol-1-sulphonate and evolution of nitrogen or formation of the nitrosoamine, although the reaction was examined under a variety of conditions. On the other hand, the compounds, for example, from *o*- and *m*-nitroaniline, 2:4-dinitroaniline, 4-nitroaniline-2-sulphonic acid, 4-chloro-2-nitroaniline, 4-nitro-2-chloroaniline, 2:6-dibromo-4-nitroaniline, and 3-nitro-4-aminotoluene give rise to the new reaction with sodium hydroxide, accompanied usually by the development of a transient intense colour, and new compounds are formed with properties similar to those of the compound derived from *p*-nitroaniline. In fact, the only compounds which have yet been found to give rise to the new reaction, and which do not contain a nitro-group, are aminoazo-compounds, such as 4-aminoazobenzene and its sulphonic acid. The suitability of a diazo-compound for participation in the new reaction depends mainly on the formation of a condensation product with  $\beta$ -naphthol-1-sulphonic acid, sufficiently stable to react further with sodium hydroxide without decomposition.

The possibility of using other compounds in place of  $\beta$ -naphthol-1-sulphonic acid was examined next. Diazotised *p*-nitroaniline condenses with  $\beta$ -naphthylamine-1-sulphonic acid, but the product does not react in the new way, nor is there any evidence of the

occurrence of the new reaction with  $\beta$ -naphthol-8-sulphonic acid or phenol-*o*-sulphonic acid. Naphthalene- $\alpha$ -sulphonic acid condenses with diazotised *p*-nitroaniline (Becker, D.R.-P. 89998) and the diazosulphonate dissolves in aqueous sodium carbonate, but the addition of sodium hydroxide to the solution causes decomposition with formation of sodium naphthalene- $\alpha$ -sulphonate and sodium *p*-nitrophenylnitrosoamine. Consequently, the presence of a hydroxyl group in the *o*-position with respect to the sulphonic group in the naphthalene nucleus is an essential feature of the new reaction. 1-Methyl- $\beta$ -naphthol condenses with diazotised *p*-nitroaniline and its *o*-sulphonic acid, probably with formation of diazo-oxides, but these also are decomposed by sodium hydroxide. Finally, there was no evidence of the occurrence of the new reaction when diazotised *p*-nitroaniline and 1-bromo- $\beta$ -naphthol were used, for the halogen atom in the latter compound is so labile that Para-red is produced under all conditions. Consequently,  $\beta$ -naphthol-1-sulphonic acid stands alone in giving rise to the new reaction.

From this point our attention has been confined to a detailed study of the compound formed by the action of an excess of sodium hydroxide on a solution of 4'-nitrobenzene-2-naphthol-1-diazosulphonate in aqueous sodium carbonate.

This compound has the formula  $C_{16}H_{12}O_7N_3SNa$  and is the sodium salt of a sulphonic acid. Aqueous solutions are decolorised by zinc dust and ammonia, and are reoxidised to a deeper colour, indicating, *inter alia*, that a nitro-group has been reduced to an amino-group. Reduction proceeds further with hydrosulphite [hyposulphite] or acid stannous chloride, and, although concordant results were obtained with difficulty in titrations with titanous chloride or sulphate, the figures indicated that 8 atoms of hydrogen were required for complete reduction as compared with 6 for the mere reduction of a nitro- to an amino-group. When an aqueous solution of the compound  $C_{16}H_{12}O_7N_3SNa$  is boiled with aqueous mineral acid, the sulphur is eliminated as sulphur dioxide, thus :



This behaviour is not confined to this compound, but is a common property of all the analogous compounds which we have yet prepared, and gave the first clue to the actual mechanism of the new reaction, for although the sulphonic group in  $\beta$ -naphthol-1-sulphonic acid is hydrolysed by similar treatment,  $\beta$ -naphthol is formed and not 1 : 2-dihydroxynaphthalene. The hydroxy-derivative has the formula  $C_{16}H_{13}O_5N_3$  and with alkaline hydrosulphite a compound  $C_{16}H_{17}O_3N_3$  is formed as the sole reduction product, *i.e.*, not only

has a nitro-group been reduced to an amino-group, but an additional two hydrogen atoms have been introduced. Reduction with acid stannous chloride, alone or in presence of granulated tin, however, gave varying results according to the duration and temperature of the reaction, and two further compounds were obtained. Closer investigation showed that whether alkaline hydrosulphite or acid stannous chloride is used, the initial reduction product is the compound  $C_{16}H_{17}O_3N_3$ . The latter, however, reacts with boiling hydrochloric acid, forming the compound  $C_{14}H_{11}ON_3$ , which is capable of undergoing further change with acid-reducing agents, forming the compound  $C_{14}H_{12}ON_2$ . Thus, although several derivatives and degradation products were obtained, we failed to bring about fission into two aromatic products by these reactions.

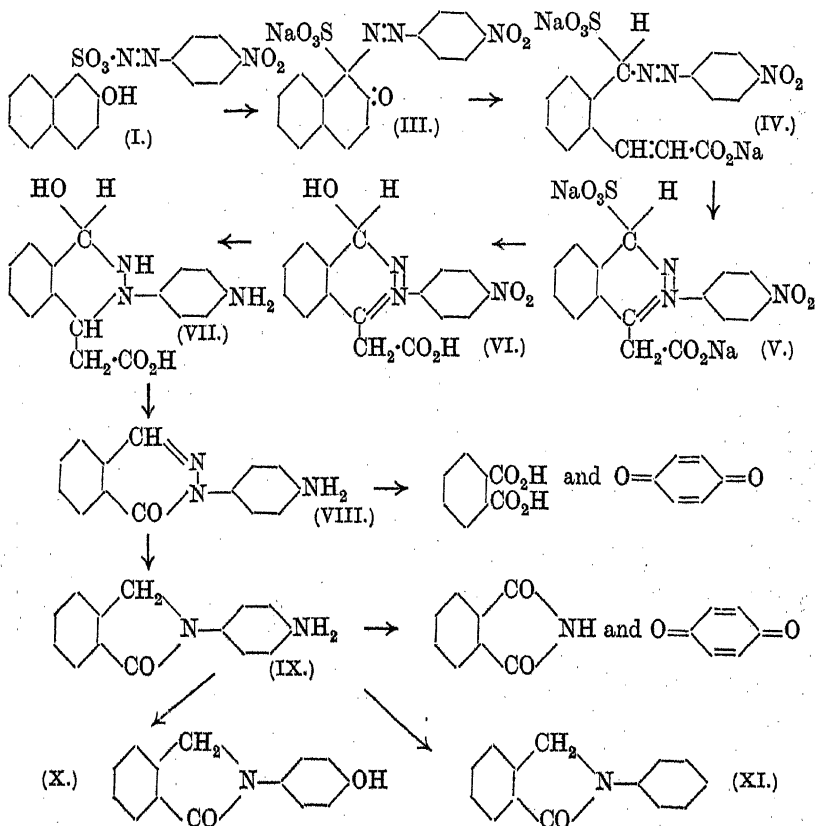
We wish to acknowledge here our great indebtedness to Professor Arthur Lapworth, F.R.S., and to Professor Robert Robinson, F.R.S., who first propounded the explanation of the mechanism of the new reaction upon which our constitutional formulæ are based, and to whom our warmest thanks are due for their interest in this investigation.

The course of the reaction in the case of 4'-nitrobenzene-2-naphthol-1-diazosulphonate (I) is outlined in the scheme on p. 695.

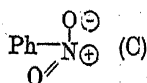
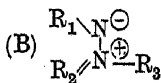
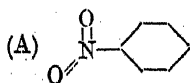
Reference has been made already to the compounds formed by the action of aqueous sodium carbonate on diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid, and regarded hitherto as diazo-oxides. It would not be anticipated that diazo-oxides would react with alkali hydroxides in the manner outlined on p. 695, and it is upon the occurrence of this new reaction and the properties of the compounds to which it leads, that our opinion is based that the former compounds are really *sodium aryl-1-azo- $\beta$ -naphthaquinone-1-sulphonates*. It is considered that sodium hydroxide opens the ring\* of *sodium 4'-nitrobenzene-1-azo- $\beta$ -naphthaquinone-1-sulphonate* (III) with addition of sodium hydroxide, forming the intermediate carboxylic acid (IV), which is not isolated, and a quinonoid modification of which would account for the transient intense coloration. The next step is a rearrangement and closing of the ring which we believe occurs as shown in (V) with formation of *disodium 3-(4'-nitrophenyl)-1:3-dihydrophthalazine-4-acetate-1-sulphonate*, and when the mixture is rendered faintly acid, the *mono-sodium* salt separates. The replacement of the sodium-1-sulphon-

\* The opening of the naphthalene ring forming a carboxylic acid has also been effected by Werner and Piguet (*Ber.*, 1904, 37, 4310), who prepared *o*-cyanocinnamic acid by the very vigorous reaction which occurs when a pyridine solution of 1-nitroso- $\beta$ -naphthol is treated with benzenesulphonyl chloride or sulphuryl chloride.

ate group by hydroxyl gives 1-hydroxy-3-(4'-nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid (VI). Formula (VI) is in agreement with the behaviour of this compound on reduction, whereby 1-hydroxy-3-(4'-aminophenyl)-tetrahydrophthalazine-4-acetic acid (VII) is formed.



N.B.—Formulae (V) and (VI) above correspond with the familiar formula for nitrobenzene (A), but the formulae may be expressed equally well as containing the semi-polar bond (B), corresponding with the form (C) for nitrobenzene.



Attempts to degrade compound (VI) by oxidation with acid dichromate were unsuccessful and gave an apparently more com-

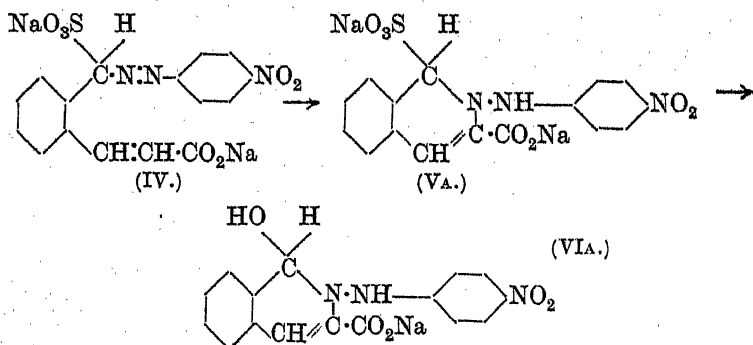
plex compound, which has been set aside for future investigation, as has also a compound formed by boiling with aqueous sulphuric acid.

The oxidation of compound (VII) with acid dichromate proceeded satisfactorily only if limited, and the compound formed has also been set aside for future investigation.

When compound (VII) is boiled with aqueous mineral acid, it is converted into 4'-amino-3-phenylphthalaz-4-one (VIII), the latter constitution being supported by the fact that oxidation with hot acid dichromate gives phthalic acid and benzoquinone.

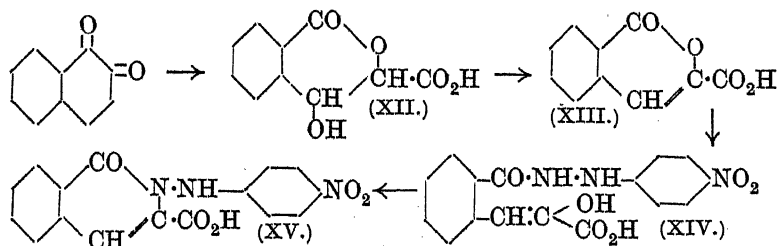
When compound (VIII) is reduced with zinc dust and hydrochloric acid, one nitrogen atom is eliminated as ammonia and 4'-amino-*N*-phenylphthalimidine (IX) is produced. Thus, this reaction is similar to that observed by Racine (*Annalen*, 1887, 239, 78) in the preparation of *N*-phenylphthalimidine (XI) from 3-phenylphthalaz-4-one by reduction with tin and hydrochloric acid. The constitution of compound (IX) was confirmed by the preparation from it of *N*-phenylphthalimidine (XI), and also by oxidation with cold acid dichromate, when phthalimide and benzoquinone were obtained. The fact that phthalimide was obtained in this case suggests that it was also the primary oxidation product of compound (VIII), but that hydrolysis then occurred at the temperature necessary for satisfactory oxidation in the latter case.

At an early stage in our investigation it appeared possible that the rearrangement and closing of the ring in passing from compound (IV) might occur with the formation of *N*-arylimino-derivatives of isoquinoline thus :



In order to determine which of the two schemes for the final stage in the reaction is correct, the compound (VI) or (VIa) was studied closely. It might be argued that a compound such as (VIa) would give *p*-phenylenediamine as one of its reduction products, whereas we failed to obtain any trace of *p*-phenylenediamine by the reduc-

tion of this compound. As the literature appeared to contain no reference to *N*-arylimino-derivatives of isoquinoline, for purposes of comparison with compound (VI) or (VIa), a related compound undoubtedly of the type of the latter was synthesised thus :

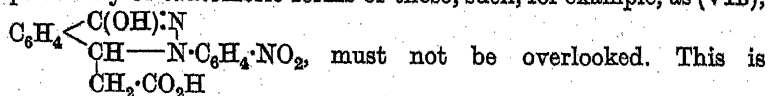


$\beta$ -Naphthaquinone was oxidised by calcium hypochlorite (Zincke and Scharfenberg, *Ber.*, 1892, 25, 399; compare Zincke, *ibid.*, 1168, 1493; Bamberger and Kitschelt, *ibid.*, 888) to the  $\delta$ -lactone of *o*-carboxyphenylglyceric acid (XII), and this was converted into isocoumarin-3-carboxylic acid (XIII) by heating with hydrochloric acid at 160—165°. It was anticipated that the latter would condense with *p*-nitrophenylhydrazine in alcoholic solution with elimination of water, forming *N*-4'-nitrophenyliminoisocarbostyryl-3-carboxylic acid (XV), as Bamberger and Frew (*Ber.*, 1894, 27, 198) prepared *N*-phenylisocarbostyryl-3-carboxylic acid in this way, using aniline. Actually, this condensation gave in our case the *hydrazone* (XIV), and the final stage of the synthesis was completed only by boiling a suspension of the latter in toluene in presence of phosphorus trichloride.

Compound (VI) or (VIa) dissolves in alkalis with a deep wine-red colour, and is reduced by hydrosulphite to compound (VII) in almost theoretical yield. Compound (XV) dissolves in alkalis with a deep red colour, but when reduced with hydrosulphite under exactly the same conditions, although no *p*-phenylenediamine could be detected and the sole reduction product was an *amino-acid*, the yield of the latter was much inferior to that obtained in the former case. This is probably due to the fact that compound (XV) is much more sensitive to alkalis than compound (VI) or (VIa). Other noteworthy differences between the properties of the two compounds were observed. Thus, whereas compound (VI) or (VIa) is esterified readily by passing hydrogen chloride through a solution in the requisite alcohol, or by means of the alcohol and sulphuric acid, or by the action of alkyl halides on the silver salt, we failed to esterify the carboxyl group in compound (XV). Further, compound (VI) or (VIa) forms an *anilide* when boiled with aniline in toluene solution in presence of phosphorus trichloride, but

compound (XV) is unaffected by this treatment. These differences in the properties of the two carboxylic acids are probably due to the proximity of the imino- and carboxyl-groups in compound (XV), and indicate the improbability of formula (VI<sub>A</sub>), particularly as we failed to prepare a nitroso-derivative of the compound, or to detect an imino-group in it by alkylation. In order to arrive at a definite conclusion on this point, the behaviour of compound (VI) or (VI<sub>A</sub>), when heated with an excess of zinc dust, was examined next, as Bamberger and Frew (*loc. cit.*) found that *N*-phenylisocarbostyryl-3-carboxylic acid gives isoquinoline when treated in this manner. In our case, however, we failed to obtain any trace of isoquinoline, a fact which appeared definitely to exclude formula (VI<sub>A</sub>). This is supported also by the fact that one of our later degradation products (VIII) undoubtedly contains two nitrogen atoms in the ring, and it is difficult to conceive how such a compound could be formed from an isoquinoline derivative. Further support of formula (VI) is afforded by the fact that when this compound is heated carefully above its melting point, nitrobenzene is formed, together with a basic residue which has not yet been examined closely; this behaviour is analogous to that of *p*-nitroazoxybenzene, which also gives nitrobenzene and a basic residue under similar conditions.

Consequently, formulæ (V<sub>A</sub>) and (VI<sub>A</sub>) have been discarded and it appears that formulæ (V) and (VI) are correct, although the possibility of tautomeric forms of these, such, for example, as (VI<sub>B</sub>),



must not be overlooked. This is virtually an isoamide of a carboxylic acid, however, and it is improbable that such a compound would be reduced by alkaline hydrosulphite in the manner shown in (VII).

In the present state of our investigation, formulæ (V) and (VI) appear the most probable and agree best with the formulæ assigned to their derivatives and degradation products which we have yet prepared, although it is possible that the former may require slight modification in the light of future work. The closing of the ring which occurs in passing from (IV) to (V) is a condensation of a type closely allied to the condensation of nitrosobenzene and ethyl methylenemalonate recently described by Burkhardt and Lapworth (*J.* 1925, 127, 1749).

Noteworthy features of the new reaction described in this communication are the simplicity and neatness with which certain naphthalene derivatives are converted into complex phthalazine derivatives. The latter by simple means are capable of almost



quantitative conversion into many other interesting compounds, which are now rendered readily accessible for further study.

Further work on this subject is in progress and the investigation will be extended in the various directions indicated.

#### EXPERIMENTAL.

*Monosodium 3-(4'-Nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid-1-sulphonate* (compare V).—A filtered solution of 48 g. of commercial sodium  $\beta$ -naphthol-1-sulphonate in 220 c.c. of water was stirred into a cold solution of diazotised *p*-nitroaniline, obtained by adding a concentrated solution of 14 g. of sodium nitrite to a solution of 24 g. of *p*-nitroaniline in 60 c.c. of concentrated hydrochloric acid and 240 c.c. of water. The 4'-nitrobenzene-2-naphthol-1-diazosulphonate (I) separated immediately as an orange precipitate in theoretical yield (calculated on the *p*-nitroaniline). This was filtered, washed free from acid with brine, made into a paste with 150 c.c. of cold water, and stirred into a cold solution of 48 g. of anhydrous sodium carbonate in 120 c.c. of water. A solution was produced but, if kept, crystals of *sodium 4'-nitrobenzene-1-azo- $\beta$ -naphthoquinone-1-sulphonate* (III) separated. The cold orange solution was added immediately to a cold solution of 40 g. of sodium hydroxide in 80 c.c. of water, the temperature rose about 15°, and the deep crimson mixture was left overnight until the colour had changed completely to yellowish-brown. It was rendered faintly acid with hydrochloric acid, then made alkaline with sodium carbonate, and a trace of Para-red filtered off. The filtrate was rendered faintly acid with hydrochloric acid and, under these conditions, the product separated completely as a yellow, semi-crystalline precipitate. (N.B.—Many experiments were carried out to determine the best conditions for the preparation of this compound, and although the yield was not affected materially, variations of temperature, excess of sodium hydroxide, and duration of the reaction, gave a resinous product which coagulated slowly.) After drying, sodium chloride was removed by extraction with absolute alcohol, from which solvent the product crystallised in orange, prismatic needles (yield 66 g.; 91.5% of the theoretical) (Found: C, 46.3; H, 2.9; N, 10.4; S, 7.5; Na, 5.2.  $C_{16}H_{12}O_7N_3SNa$  requires C, 46.5; H, 2.9; N, 10.2; S, 7.7; Na, 5.5%). It is readily soluble in water, but less soluble in alcohol, forming yellow solutions, which are deepened by the addition of alkalis. The aqueous solution is decolorised by zinc dust and ammonia, and on exposure to air a deeper colour returns. It is a level-dyeing, pure greenish-yellow acid dye of good tinctorial power and of good fastness to other influences, but fugitive to light, even when dyed

in admixture with a fast blue. When heated with concentrated nitric acid at  $105^{\circ}$  in a sealed tube for 8 hours, decomposition occurs and picric acid was isolated in yellow needles, m. p.  $122^{\circ}$ .

*1-Hydroxy-3-(4'-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic Acid* (VI).—A solution of 32 g. of monosodium 3-(4'-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid 1-sulphonate in 120 c.c. of water was boiled with 64 c.c. of concentrated hydrochloric acid (aqueous sulphuric acid also can be used) until evolution of sulphur dioxide had ceased, and the product, which separated first as an oil, had formed yellowish-brown crystals. The latter were washed with boiling water and crystallised from ethyl acetate in pale yellow, vitreous, irregular prisms, m. p.  $241^{\circ}$  (yield 24 g.; 94%). Sulphur dioxide evolved during the reaction was determined quantitatively in the usual manner and was equivalent to one molecular proportion (Found: C, 58.9; H, 4.2; N, 12.8.  $C_{16}H_{13}O_5N_3$  requires C, 58.7; H, 4.0; N, 12.8%). When the substance was heated carefully above its melting point, nitrobenzene (confirmed by conversion into aniline) was obtained, together with a basic residue which has not yet been examined closely. This behaviour is analogous to that of *p*-nitroazoxybenzene, which also gives nitrobenzene under similar conditions. The substance is readily soluble in alcohol, acetone, or glacial acetic acid, but less soluble in benzene or ether. It is sparingly soluble in water, forming a solution acid to litmus, but dissolves readily in sodium carbonate or hydroxide with a deep wine-red colour, and prolonged boiling of the alkaline solution causes decomposition. It forms a reddish-brown *silver* salt and a yellowish-brown *barium* salt, and decolorises bromine water. It dissolves in cold concentrated sulphuric acid with an orange colour and is reprecipitated unaltered on dilution, but when 5 g. were dissolved in 50 c.c. of sulphuric acid, then diluted with 60 c.c. of water, and the solution boiled under reflux for 1 hour, there was no precipitate on further dilution. A substance (4 g.) was isolated and crystallised from alcohol in fine yellow needles, m. p.  $331^{\circ}$ , but this has not yet been examined closely.

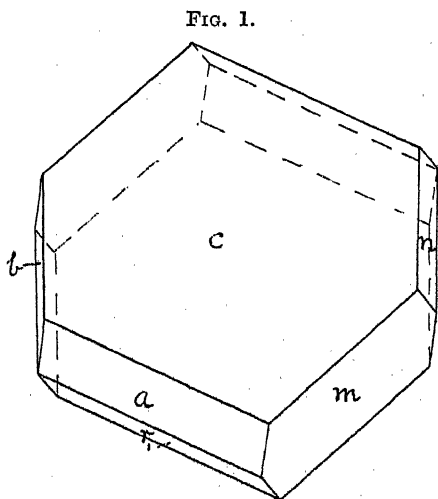
*Derivatives of 1-Hydroxy-3-(4'-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic Acid.*—*Methyl ester.* A solution of 5 g. in 50 c.c. of dry methyl alcohol was saturated with dry hydrogen chloride at  $0^{\circ}$ , left over-night, and then boiled under reflux for 2 hours. The *ester* crystallised from methyl alcohol in yellow prisms, m. p.  $153^{\circ}$  (Found: C, 59.8; H, 4.6; N, 12.5.  $C_{17}H_{15}O_5N_3$  requires C, 59.8; H, 4.4; N, 12.3%). *Ethyl ester.* (a) A solution of 3 g. in 30 c.c. of dry ethyl alcohol was boiled with 1.5 g. of concentrated sulphuric acid under reflux for 4 hours. (b) The dry, reddish-brown, amorph-

ous silver salt, precipitated by the addition of silver nitrate to a neutral solution of 5 g. in sodium hydroxide, was boiled with 2 g. of ethyl iodide and 50 c.c. of dry ethyl alcohol under reflux for 1 hour. (c) As described above for the methyl ester, except that 60 c.c. of dry ethyl alcohol were used. The three products were identical in all respects and crystallised from ethyl alcohol in yellow crystals, tabular in character and with hexagonal outline; m. p.  $180^{\circ}$ . We have been furnished with the following crystallographic description of the substance by Mr. H. E. Buckley of the Department of Crystallography, University of Manchester, to whom we express our grateful thanks:

"The symmetry is anorthic (triclinic) pinacoidal, with  $a : b : c = 1.387 : 1.0626$  and  $\alpha = 78^{\circ} 15'$ ,  $\beta = 40^{\circ} 10'$ ,  $\gamma = 117^{\circ} 6'$ .

The forms usually developed are  $a(100)$ ,  $b(010)$ ,  $c(001)$ , tabular,  $n(011)$  and  $r(\bar{1}01)$  (Fig. 1).

Angles measured:  $a : b = 118^{\circ} 11'$ ,  $a : c = 39^{\circ} 42'$ ,  $a : m = 54^{\circ} 53'$ ,  $c : m = 56^{\circ} 42'$ ,  $c : n = 57^{\circ} 53'$ ,  $c : b = 103^{\circ} 19'$ ,  $n : r = 68^{\circ} 19'$ ,  $m : n = 35^{\circ} 45'$ , and  $c : r = 89^{\circ} 10'$ " (Found: C, 61.1; H, 4.7; N, 12.1.  $C_{18}H_{17}O_5N_3$  requires C, 60.8; H, 4.8; N, 11.8%). It dissolves



in sodium carbonate with an orange-brown colour, and is hydrolysed to the original acid by boiling with alcoholic potassium hydroxide. Attempts to acetylate the ester gave a yellow, resinous product which could not be crystallised. *Acetyl derivative*. A solution of 5 g. of the acid in 10 c.c. of glacial acetic acid was boiled with 5 c.c. of acetic anhydride under reflux for 8 hours, and then poured on to ice. The *acetyl* derivative crystallised from ethyl alcohol in greenish-yellow, vitreous prisms, m. p.  $212^{\circ}$  (Found: C, 58.8; H, 4.2; N, 11.7.  $C_{18}H_{15}O_6N_3$  requires C, 58.5; H, 4.1; N, 11.4%). It dissolves in sodium carbonate with an orange-brown colour or in sodium hydroxide with a wine-red colour, and attempts to esterify it gave resinous products which could not be crystallised. *Anilide*. A fine suspension of 4 g. of the acid in 400 c.c. of toluene was boiled with 2.3 g. of aniline and 1 g. of

phosphorus trichloride under reflux for 5 hours with stirring. When cold, the residue was washed with a little sodium carbonate and, after several crystallisations from ethyl acetate, formed yellow needles, m. p. 190—192° (decomp.) (Found : C, 65.4; H, 4.6; N, 13.9.  $C_{22}H_{18}O_4N_4$  requires C, 65.7; H, 4.5; N, 13.9%). The anilide dissolves in sodium hydroxide with a red colour and is hydrolysed to the original acid by boiling concentrated hydrochloric acid. *Oxidation of (VI)*. A fine suspension, obtained by dissolving 20 g. in 200 c.c. of cold concentrated sulphuric acid and pouring on to 800 g. of ice, was oxidised by adding gradually 10 g. of powdered sodium dichromate. Next day the product was precipitated completely by nearly neutralising with sodium hydroxide and, after several crystallisations from ethyl alcohol and ethyl acetate, yellow leaflets (11.5 g.), m. p. 247°, were obtained, but this substance requires further investigation.

*1-Hydroxy-3-(4'-aminophenyl)-tetrahydrophthalazine-4-acetic Acid (VII)*.—Hydrosulphite was added to a solution of 12 g. of 1-hydroxy-3-(4'-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid in 150 c.c. of water and 10 g. of sodium hydroxide at about 90° until the deep wine-red colour had disappeared, the mixture being kept alkaline throughout by the addition of sodium hydroxide. The yellow solution was filtered and, if the filtrate was cooled, fine yellow needles of the *sodium* salt separated incompletely. The product was best isolated, therefore, by the addition of hydrochloric acid until a white precipitate had separated completely. The end-point is readily determined, because too much acid redissolves the precipitate with a brown colour. It was washed with cold water and crystallised from a large volume of boiling water in colourless prisms, m. p. 239° (yield 10.7 g.; 97.5%) (Found : C, 64.3; H, 5.7; N, 14.2.  $C_{16}H_{17}O_3N_3$  requires C, 64.2; H, 5.7; N, 14.0%). This compound can also be obtained by rapid reduction with acid stannous chloride, but the yield is not so good owing to the subsequent action of acid upon it. It is soluble in alcohol, insoluble in benzene, and gives a transient wine-red colour with ferric chloride. It dissolves readily in dilute alkalis or dilute acids and can be diazotised. The esters could not be obtained by the reduction of the esters of 1-hydroxy-3-(4'-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid with alkaline hydrosulphite, for hydrolysis also occurred, nor did direct esterification prove satisfactory. The fact that the compound is affected by acids interfered with the preparation of a pure *acetyl* derivative, for, after crystallisation from dilute acetic acid, colourless plates, softening at 145—165° and melting sharply at 266°, were obtained (Found : C, 64.3; H, 5.2; N, 12.3.  $C_{18}H_{19}O_4N_3$  requires C, 63.3; H, 5.6;

N, 12.3%). *Oxidation of (VII).* Powdered sodium dichromate (7 g.) was added in small portions during 3 hours to a solution of 20 g. in 400 c.c. of water and 100 c.c. of concentrated sulphuric acid at the air temperature. A transient wine-red colour was produced after each addition, but any further addition did not produce this colour. The mixture was rendered just alkaline with sodium hydroxide, diluted with water to 2 litres, boiled, filtered, the filtrate neutralised, and concentrated. After crystallisation from alcohol and then from water, yellow, prismatic needles (15 g.), m. p.  $276^{\circ}$ , were obtained, but this substance requires further investigation.

*4'-Amino-3-phenylphthalaz-4-one (VIII).*—A solution of 12 g. of 1-hydroxy-3-(4'-aminophenyl)-tetrahydrophthalazine-4-acetic acid in 300 c.c. of concentrated hydrochloric acid (25–30% aqueous sulphuric acid also can be used) was boiled under reflux. A less soluble *hydrochloride* separated progressively in colourless needles after 1 hour and the reaction was completed by boiling for 18 hours. After cooling, the hydrochloride was filtered off and converted into the base, which crystallised from alcohol in deep straw-coloured, prismatic needles, m. p.  $259^{\circ}$  (yield 8.8 g.; 92.5%) (Found: C, 71.0; H, 4.7; N, 17.8.  $C_{14}H_{11}ON_3$  requires C, 70.9; H, 4.6; N, 17.7%). It is soluble in hot water, insoluble in alkalis, but soluble in dilute acids and can be diazotised, although we have not yet succeeded in removing the amino-group or replacing it by a hydroxyl group without the compound undergoing further change. *Acetyl derivative.* A solution of 1 g. in 10 c.c. of glacial acetic acid was boiled with 0.5 c.c. of acetic anhydride. After a few minutes the colourless acetyl derivative separated completely; it crystallised from a large volume of boiling water in almost colourless plates, m. p.  $348^{\circ}$  (Found: C, 68.9; H, 4.8; N, 14.9.  $C_{18}H_{13}O_2N_3$  requires C, 68.8; H, 4.7; N, 15.0%). *Oxidation of (VIII).* A solution of 5 g. in 400 c.c. of water and 80 c.c. of concentrated sulphuric acid was oxidised at the air temperature by adding gradually 16 g. of powdered sodium dichromate. A brown precipitate separated and next day benzoquinone, yellow needles, m. p.  $115^{\circ}$ , was isolated by extraction with ether. The other oxidation product could not be obtained satisfactorily under these conditions, but was obtained in a second oxidation in which a further 14 g. of dichromate were added and the mixture heated. In this case extraction with ether gave phthalic acid, colourless needles, m. p.  $197^{\circ}$  (confirmed by conversion into phthalic anhydride, colourless needles, m. p.  $129^{\circ}$ , and by the formation of fluorescein).

*4'-Amino-N-phenylphthalimidine (IX).*—A solution of 20 g. of 4'-amino-3-phenylphthalaz-4-one in 1 litre of water and 100 c.c. of

concentrated hydrochloric acid was boiled, and 300 c.c. of concentrated hydrochloric acid were added, followed by 30 g. of zinc dust in small portions during  $2\frac{1}{2}$  hours with vigorous boiling so that the volume was reduced to 700 c.c. After cooling, the product separated completely as colourless plates of the *hydrochloride*, together with a small proportion of colourless needles of the *zinc double chloride*. Completion of the reaction was indicated by the pink colour of the filtrate, and the latter contained ammonia. The crystals were dissolved in a little hot water and hydrochloric acid, the solution was rendered alkaline, and the dry precipitate extracted with alcohol. The base crystallised in almost colourless, prismatic needles, m. p.  $198^{\circ}$  (yield 16.5 g.; 87%) (Found: C, 75.1; H, 5.5; N, 12.4.  $C_{14}H_{12}ON_2$  requires C, 75.0; H, 5.4; N, 12.5%). *Acetyl derivative*. A solution of 1 g. in 10 c.c. of glacial acetic acid was boiled with 0.5 c.c. of acetic anhydride and poured into water; the product crystallised from dilute acetic acid in fine, colourless needles, m. p.  $196^{\circ}$  (Found: C, 72.0; H, 5.5; N, 10.7.  $C_{16}H_{14}O_2N_2$  requires C, 72.2; H, 5.4; N, 10.5%). *Oxidation of (IX)*. This was effected as described in the first example under oxidation of (VIII), except that a fine suspension of the *sulphate* was used, and dark green needles separated at first and disappeared subsequently. Ether extraction gave benzoquinone, yellow needles, m. p.  $115^{\circ}$ . The other oxidation product was obtained best in a second oxidation in which a further 16 g. of dichromate were added at the air temperature. In this case extraction with ether gave phthalimide, flat, colourless needles, m. p.  $234^{\circ}$  (confirmed by conversion into phthalamide, colourless crystals, m. p.  $222^{\circ}$  with evolution of ammonia and reformation of the imide).

*N-Phenylphthalimidine (XI)*.—A fine suspension of the sulphate, obtained by grinding 10 g. of the amino-derivative with sulphuric acid, was diazotised with a concentrated solution of 3.6 g. of sodium nitrite. The sparingly soluble *diazo-sulphate*, almost colourless needles, was boiled with 1 litre of alcohol until the evolution of nitrogen had ceased; the *N*-phenylphthalimidine crystallised in almost colourless plates, m. p.  $160^{\circ}$  as given by Racine (*loc. cit.*)

*4'-Hydroxy-N-phenylphthalimidine (X)*.—A fine suspension of the hydrochloride, obtained by grinding 20 g. of the amino-derivative with 36 c.c. of concentrated hydrochloric acid and 800 c.c. of water, was diazotised with a concentrated solution of 7.2 g. of sodium nitrite. Carbamide was added to remove excess nitrous acid, the solution poured into 640 c.c. of dilute sulphuric acid (1:3) at  $90^{\circ}$ , and the mixture boiled for 2 hours until the stable diazo-compound had decomposed completely. The hydroxy-

derivative crystallised from alcohol in colourless needles, m. p. 228° (yield 18.2 g.; 90.5%) (Found: C, 74.8; H, 5.1; N, 6.1.  $C_{14}H_{11}O_2N$  requires C, 74.7; H, 4.9; N, 6.2%). *Methyl ether*. A solution of 2 g. in 50 c.c. of dry methyl alcohol was boiled with methyl iodide and sodium. The ether crystallised from methyl alcohol in colourless plates, m. p. 134° (Found: C, 75.2; H, 5.5; N, 6.0.  $C_{15}H_{13}O_2N$  requires C, 75.3; H, 5.4; N, 5.9%). The *ethyl ether* crystallised from ethyl alcohol in colourless needles, m. p. 148° (Found: C, 75.7; H, 5.9; N, 5.6.  $C_{16}H_{15}O_2N$  requires C, 75.9; H, 5.9; N, 5.5%).

*N-4'-Nitrophenyliminoisocarbostyryl-3-carboxylic Acid* (XV).— $\beta$ -Naphthaquinone (3 g.) was oxidised by calcium hypochlorite to the  $\delta$ -lactone of *o*-carboxyphenylglyceric acid (2 g.) (XII), colourless leaflets, m. p. 202—203°, as described by Zincke and Scharfberg (*loc. cit.*), who give m. p. 202°, whereas Bamberger and Kitschelt (*loc. cit.*) give m. p. 204.5°. This acid (12 g.) was heated with concentrated hydrochloric acid (60 c.c.) at 160—165° and gave *isocoumarin-3-carboxylic acid* (8.2 g.) (XIII), colourless, quadrilateral plates, m. p. 238—239° (Zincke, *Ber.*, 1892, 25, 1493 gives m. p. 235°, whereas Bamberger and Kitschelt give m. p. 237°). An alcoholic solution of *isocoumarin-3-carboxylic acid* (5 g.) and *p*-nitrophenylhydrazine (4.05 g.) was boiled under reflux for  $\frac{1}{2}$  hour, and gave *o*-carboxy- $\alpha$ -hydroxycinnamic acid *p*-nitrophenylhydrazide (8.5 g.) (XIV), which crystallised from alcohol in fibrous, yellow needles, m. p. 189—190° (decomp.) (Found: C, 55.9; H, 4.0; N, 12.5.  $C_{16}H_{13}O_6N_3$  requires C, 56.0; H, 3.8; N, 12.2%). The hydrazide is hydrolysed into its constituents by heating with dilute mineral acids. The elements of water were removed by boiling the finely divided hydrazide (4 g.) suspended in toluene (800 c.c.) with phosphorus trichloride (1 g.) under reflux for 5 hours. *N-4'-Nitrophenyliminoisocarbostyryl-3-carboxylic acid* (2.24 g.) crystallised from ethyl acetate in small, pale yellow needles, m. p. 287° (decomp.). This compound is formed also by condensing *isocoumarin-3-carboxylic acid* with *p*-nitrophenylhydrazine in presence of phosphorus trichloride and boiling toluene, but the yield is much inferior (Found: C, 58.8; H, 3.6; N, 13.0.  $C_{18}H_{11}O_5N_3$  requires C, 59.1; H, 3.4; N, 12.9%). It is readily soluble in acetone or glacial acetic acid, but less soluble in alcohol or ether, and dissolves in alkalis with a deep red colour, the alkaline solution decomposing when heated. It is unaltered by boiling with dilute mineral acids, and is neither esterified nor converted into an anilide when treated under the conditions described for the preparation of these derivatives of 1-hydroxy-3-(4'-nitrophenyl)-1:3-dihydrophthalazine-4-acetic acid (VI). Reduction of the acid (4 g.) with alkaline hydro-

sulphite gave an *amino-acid* (2 g.), almost colourless, crystalline powder, m. p.  $265^{\circ}$ , which was not examined closely, and no trace of *p*-phenylenediamine could be detected in the reduction mixture.

We desire to thank (1) the Society of Dyers and Colourists for a grant which enabled one of us (A. C. B.) to take part in this investigation, and also for permission to publish the detailed results elsewhere than in the Journal of that Society, (2) Professor F. L. Pyman, F.R.S., for his kindly interest during the progress of the investigation, and (3) Alliance Colour and Chemical Co., British Dyestuffs Corporation, and the Gas Light and Coke Co., for gifts of sodium  $\beta$ -naphthol-1-sulphonate.

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## XCVII.—*Absorption Spectra and Tautomerism. Part I.* *Keto-enol Tautomerism. Ethyl Acetoacetate, Acetyl- acetone, and $\alpha$ -Benzoylcamphor.*

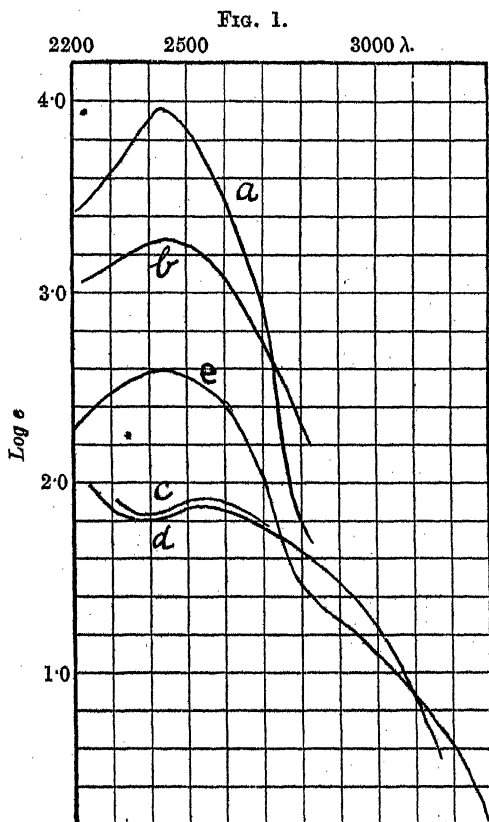
By RICHARD ALAN MORTON and WILLIAM CHARLES VICTOR  
ROSNEY.

ALTHOUGH the absorption spectra of ethyl acetoacetate and its derivatives have been studied repeatedly (Baly and Desch, J., 1904, 85, 1029; Stewart and Baly, J., 1906, 89, 489; Hantzsch, Ber., 1911, 44, 1771; Hantzsch and Voigt, Ber., 1912, 45, 85; Baly and Rice, J., 1913, 103, 91; Morgan and Reilly, J., 1913, 103, 1494; Bielecki and Henri, *Compt. rend.*, 1913, 156, 1332; 1914, 158, 866; Ber., 1913, 46, 3627; Hantzsch, Ber., 1912, 43, 3029), a reconsideration of the problem of the origin of their absorption bands is called for in view of the improved experimental methods which are now available (compare Grossmann, *Z. physikal. Chem.*, 1914, 109, 305).

The vapour from ethyl acetoacetate, cooled to  $-80^{\circ}$  in order to reduce the vapour pressure, shows an absorption band, without fine structure, at  $\lambda_{(\max.)} = 2381 \text{ \AA.}$ ,  $e_{(\max.)} = 1000$  (approx.). Thin layers of the liquid ester show a band at  $\lambda_{(\max.)} = 2430$ ,  $e_{(\max.)} = 367$ , and the same band appears in solutions in ether, alcohol ( $e = 2000$ ), and hexane ( $e = 9100$ ). Since the ratio  $e_{\text{alcohol}}$  to  $e_{\text{hexane}}$  agrees excellently with the relative content of enol in the solutions as measured by the addition of bromine, the band at  $2430 \text{ \AA.}$  may be ascribed to the enol. This band is shifted to  $2550 \text{ \AA.}$  in ethyl ethylacetoacetate,  $\text{CH}_3\text{-C(OH):C(OC}_2\text{H}_5\text{)-CO}_2\text{Et}$ , and to  $2348 \text{ \AA.}$  in ethyl  $\beta$ -ethoxycrotonate,  $\text{CH}_3\text{-C(OEt):CH-CO}_2\text{Et}$ .



Aqueous solutions of ethyl acetoacetate, which appear to be mainly ketonic since they do not absorb bromine appreciably, give a band at 2550 Å., which is nearer to the enolic band than to the undoubtedly ketonic band of acetone at 2747 Å. Its absorptive power,  $e = 81$ , is intermediate between those of acetone (17.2) and liquid ethyl acetoacetate (367). Since a displacement of 100 Å. is often produced by a change of solvent, there is as much

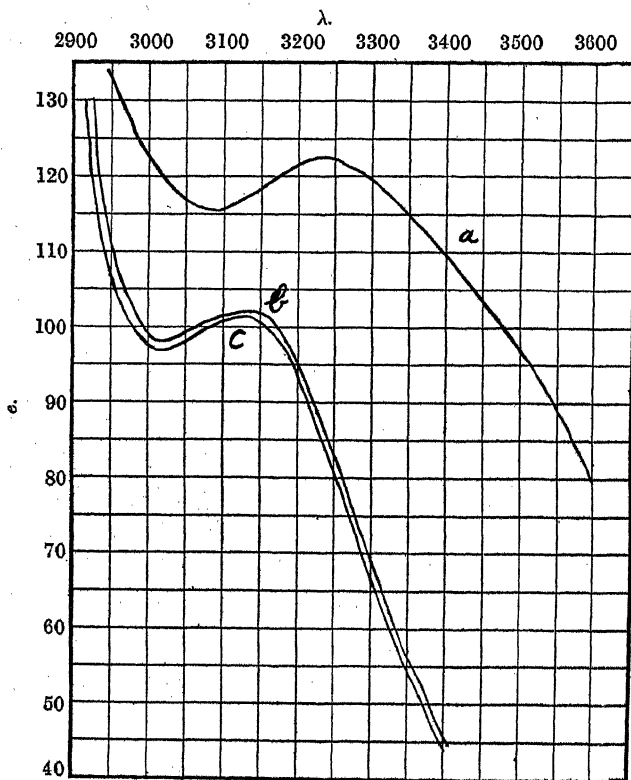


*Ethyl acetoacetate (a) in hexane, (b) in alcohol, (c) in dilute hydrochloric acid, (d) in water, (e) liquid.*

reason to ascribe the band at 2550 Å. to a trace of enol as to a large amount of ketone. There is, however, an inflexion in the curves for the liquid ester and for its solution in hexane, which may be due to an incipient ketonic band at 2700–2800 Å. This conclusion is confirmed by the fact that the liquid dialkylacetoacetic esters exhibit well-defined bands near 2900 Å., which are weakened on the addition of alcohol, but reappear when alkali is

added. Moreover, analogy with other ketones would lead us to predict a band in ethyl acetoacetate at about 2750 Å. and  $e_{(\max.)}$  about 100. Since in hexane, where 80% of the ester is enolic,  $e_{(\max.)}$  is 9100, the value for the pure enol must then be about 100 times greater than for the pure ketone. We therefore conclude that the band at 2430 Å. can be attributed to the enolic form and

FIG. 2.



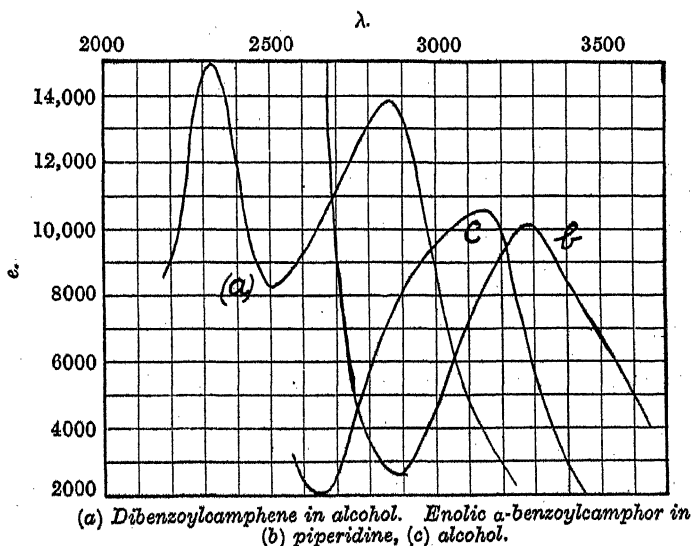
Ketonic  $\alpha$ -benzoylcamphor in (a) piperidine, (b) chloroform, and (c) alcohol.

that the ketonic form possesses a weak band near 2700 Å., which is usually masked by the stronger absorption of the enol.

Acetylacetone, which is too absorbent to be examined in the liquid state, gives a strong band at 2750 Å. in aqueous and alcoholic solutions. The ratio of the molecular extinction coefficients,  $8920/2200 = 4.05$ , agrees with the ratio 4.2 of the enol content of these solutions as measured by K. H. Meyer. The band appears, therefore, to be due to the enol, although its wave-length corresponds with that of the acetone band at 2747 Å. Since hexa-

methylacetone shows the usual ketonic band, even when very carefully purified (Rice, *Proc. Roy. Soc.*, 1914, *A*, **91**, 76), and the weak bands of the dimethyl- and diethyl-acetoacetic esters could not have been detected in presence of strongly absorbing enolic impurities, it is clear that the ketonic band cannot be attributed to the presence of a trace of enol in all ketones. It is therefore necessary to conclude that the enolic form of acetylacetone gives a band at the same wave-length as the ketonic form. This conclusion is confirmed by the facts that addition of alkali to acetone (which presumably gives rise to a trace of an enolic salt) increases the intensity of the band but does not produce a new band, and

FIG. 3.



that the two isomeric forms of benzoylcamphor give bands at the same wave-length but of unequal intensity.

Formation of a new compound from acetone by addition of alkali must result in a redistribution of selective absorption. If the compound exhibits a new absorption band, the number of acetone molecules absorbing at 2747  $\text{\AA}$ ., and therefore  $e_{(\text{max.})}$ , should decrease. The reverse is observed, so that whatever the nature of the new absorbing entity its position of maximum absorption must coincide with that of acetone itself. The data on acetone are thus in agreement with the view that enolic and ketonic modifications possess the same wave-length of maximum absorption. Since the enolic sodium salt can be present only in minute amount,

the enolic form must have a high molecular extinction, as otherwise no increase would have been observed.

The effect of alkali on ethyl acetoacetate and acetylacetone is more complicated, new bands being developed, with high extinction coefficients varying directly as the ratio of alkali to ester up to a molecular ratio of 100 : 1.

Alkaline solutions of ethyl acetoacetate were rapidly neutralised and the bromine addition was measured immediately. Although the nature of the experiments precluded reproducible quantitative data, the concurrent increases of the alkali/ester ratio and of  $\epsilon_{(\max)}$  were accompanied by an increased capacity for bromine addition. Hence the bands at 2430 and 2725 Å. for ethyl acetoacetate, and the bands at 2750 and 2913 Å. for acetylacetone, all correspond with enolic substances.

The substitution of potassium, lithium or other metals for sodium causes a small shift in the position of maximum absorption which is roughly proportional to the atomic weight of the substituent. We can therefore infer  $\lambda_{(\max)}$  when hydrogen replaces sodium. The position of such a band for ethyl acetoacetate would be nearer 2700 Å. in alcoholic solution, *i.e.*, the enolic ester corresponding with the enolic sodium salt would display the same position of maximum absorption as the ketonic tautomeride. In acetylacetone, the normal ketonic substance has already been shown to absorb at the same wave-length as the ordinary enolic form. The hypothetical enolic form of acetylacetone would, however, show a band different from that of the ketonic form.

Much valuable work has been done in recent years leading to a ringed, chelate, co-ordinated or polar structure for the metallic derivatives of acetylacetone. From the present work, it is evident that the free enolic tautomerides are different from the metallic derivatives in a very distinct way. The free enol does not give the same band as the metallic salts. It therefore seems erroneous to picture the free enol as co-ordinated or ringed in structure (compare Lowry, *Trans. Faraday Soc.*, 1924, 18, 495, 537).

The views advanced may be subjected to a fairly rigorous test by the isolation and examination of pure ketonic and enolic tautomerides. The isolation of such forms of ethyl acetoacetate can be accomplished by aseptically distilling from evacuated quartz vessels. Unfortunately, it proved quite impossible to retain the purity of thin films of the liquids between quartz plates for the period of time necessary to secure absorption spectra photographs.

The tautomeric forms of benzoylcamphor exhibit the same frequency of maximum absorption, but differ widely in absorptive power. The molecular extinction coefficients of the ketonic form

and of camphor are of the same order (34—100), and the extinctions of the enolic modification and of dibenzoylcamphene are of the order 10,000—14,000. Addition of alkali causes the appearance of a new band, which confirms the view advanced by Lowry that the metallic salts of  $\alpha$ -benzoylcamphor are co-ordinated compounds.

### Summary of Results.

Substance.	$\lambda$ (max.).	$\epsilon$ (max.).	Remarks.
Ethyl acetoacetate, vapour .	2381	ca. 1000	No fine structure.
" " liquid ...	2430	367	
" " in ether .	2430	High.	
" " in alcohol	2430	2000	Confirming Henri.
" " in hexane	2430	9100	" "
" " in water	2550	81.3	" "
" " in dil. HCl	2550	80	" "
" " in NaOH	2725	11,500	Extinction varies as recorded.
Ethyl acetoacetate in alc. NaOEt .....	2725	29,500	Extinction varies with alkali/ester ratio.
Ethyl acetoacetate in alc. HCl	2430	2,000	
" " in dil. aq. KOH .....	2743	High.	Max. varies with alkali/ester ratio.
Ethyl acetoacetate in LiOH	2707	High.	Max. varies with alkali/ester ratio.
" " in piperidine (anhydrous) .....	2735	150	Low extinction in ketonising solvent.
Cu derivative of ethyl acetoacetate .....	2736	10,000	
Al derivative in heptane .....	2684	High.	Extinction of the order 10,000.
" " in alcohol .....	2687	High.	
Mg compd. in alcohol .....	2687	High.	
Ethyl ethylacetoacetate, pure liquid .....	2550	400	
Ethyl ethylacetoacetate in alcohol .....	2550	680	Henri records max. at 2341.
Ethyl ethylacetoacetate in water .....	2700	Low.	
Ethyl ethylacetoacetate in dil. NaOH .....	2740	10,000	
Ethyl ethylacetoacetate in alc. NaOEt .....	2810	20,000	
Ethyl ethylacetoacetate in piperidine .....	2695	Uncertain.	
Ethyl ethylacetoacetate, vapour .....	ca. 2380		No fine structure.
Ethyl methylacetoacetate in alcohol .....	2520		Hantzsch's data ( <i>loc. cit.</i> ) measured from published curves.
Ethyl methylacetoacetate in water .....	2680		
Ethyl methylacetoacetate in alkali .....	2825		
Ethyl $\beta$ -ethoxycrotonate, vapour .....	2275	Uncertain.	

Substance.	$\lambda$ (max.).	$\epsilon$ (max.).	Remarks.
Ethyl $\beta$ -ethoxycrotonate, liquid .....	Indications of band near 2050.		
Ethyl $\beta$ -ethoxycrotonate in alcohol .....	2348	2880	
Ethyl $\beta$ -ethoxycrotonate in alc. NaOEt .....	2348	1820	
Ethyl dimethylacetoacetate, liquid .....	2837	Low.	Film too thin to allow of reproducible values of $\epsilon$ .
Ethyl dimethylacetoacetate in alcohol .....	Inflection only.		
Ethyl dimethylacetoacetate in alc. NaOEt .....	2840		
Ethyl dimethylacetoacetate in water .....	Inflection only.		
Ethyl dimethylacetoacetate in aq. NaOH .....	2760		
Ethyl dimethylacetoacetate in piperidine .....	Inflection only.		
Ethyl diethylacetoacetate, liquid .....	2848	Low.	
Ethyl diethylacetoacetate in alcohol, water, or piperidine .....	Inflections only.		
Ethyl diethylacetoacetate in aq. NaOH .....	2762		
Ethyl diethylacetoacetate in alc. NaOEt .....	2850		
Acetylacetone, liquid .....	Continuous end absorption.		
„ in water .....	2750	2200	
„ in alcohol ...	2748	9000	
„ in dil. HCl ...	2750	2000	
„ in aq. LiOH .....	2917	} Order 20,000	Extinction varies with alkali/ester ratio.
„ in aq. NaOH .....	2926		
„ in aq. KOH .....	2935		
„ in aq. RbOH .....	2967		
„ in piperidine (anhydrous) .....	2955	Not measured owing to difficulties of manipulation.	
„ in alc. NaOEt .....	2927	19,500	
Camphor in alcohol .....	2840	34	
Dibenzoylcamphene in alcohol .....	2860	13,700	
	2365	15,100	
$\alpha$ -Benzoylcamphor, ketonic modification in alcohol ...	3130-3145	103	
$\alpha$ -Benzoylcamphor, ketonic modification in chloroform .....	3125	104	
$\alpha$ -Benzoylcamphor, ketonic modification in piperidine .....	3240	123	
$\alpha$ -Benzoylcamphor, enolic modification in alcohol ...	3150	10,600	
$\alpha$ -Benzoylcamphor, enolic modification in piperidine .....	3280	10,300	
$\alpha$ -Benzoylcamphor, enolic modification in alc. NaOEt .....	3275	15,250	
Benzoylcamphor, ketonic modification freshly dissolved in alc. NaOEt .....	3072	1380	
Same solution after standing .....	2750	1040	
Same solution after some days .....	3275	4000	
	3270	12,300	

The following maxima have been measured for metallic derivatives of acetylacetone :

Metal.	Solvent.	$\lambda$ (max.).	Metal.	Solvent.	$\lambda$ (max.).
Cu	Alcohol	2435 and 2965	Th	Alcohol	2840
"	Heptane	2445 2970	"	Heptane	2735
Be	Alcohol	2930	"	Ammonia +	2960
Fe <sup>III</sup>	Alcohol	2730 3525 4350	"	alcohol	2960
"	Heptane	2720 3527 4340	Al	Alcohol	2893
Mg	Alcohol	2837	"	Heptane	2875

Some of the results are recorded as supplementing the work of Lowry and Desch (J., 1909, **95**, 807), Morgan and Moss (J., 1914, **105**, 189), and French (*Proc. Roy. Soc.*, 1924, **A**, **106**, 489).

The present investigation was completed before the appearance of Grossmann's work (*loc. cit.*). Whilst our experimental data are on the whole in excellent agreement with those of this investigator, some important differences may be noted. Grossmann does not record the fact that thin films of ethyl acetoacetate exhibit a band at 2430 Å., and the existence of a band in the dialkylacetoacetic esters appears to have escaped his notice.

We wish to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for maintenance grants during a part of the time occupied by the work, and to Professor E. C. C. Baly, C.B.E., F.R.S., for much guidance and encouragement.

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### XCVIII. — *Absorption Spectra and Tautomerism.* *Part II. Ethyl Mesityloxidoxalate, Formylphenyl-* *acetate, and Diacetylsuccinate.*

By RICHARD ALAN MORTON and EDWARD ROGERS.

#### *Ethyl Mesityloxidoxalate.*

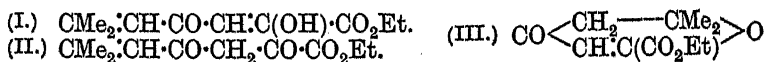
THREE modifications of ethyl mesityloxidoxalate have been isolated: (i)  $\alpha$ , m. p. 21°; (ii)  $\beta$ , m. p. 59—60°; (iii) a dimeric form, m. p. 175° (Federlin, *Annalen*, 1907, **356**, 261). These can be converted into one another as follows :

$\beta \rightleftharpoons \alpha$  in the dark, equilibrium being reached after about 12 weeks.

$\alpha \rightarrow \beta \rightarrow$  dimeride in diffuse daylight, with precipitation of the dimeride from most solvents.

The  $\alpha$ -form develops a red colour with ferric chloride and is undoubtedly the enolic form (I). Claisen at first regarded the

$\beta$ -form as a dihydropyrone derivative (III) (*Ber.*, 1891, 24, 116), but later he formulated it as the ketone (II).



Dieckmann (*Ber.*, 1920, 53, 1772) regards the  $\alpha$ -form as enolic, but rejects the ketonic formula for the  $\beta$ -form, on the ground that the small percentage of enol in the equilibrium mixture is not in accordance with Claisen's rule that the velocity of enolisation and the enol content of the equilibrium mixture increase with increasing acidity of the acyl groups: moreover, the  $\alpha$ -ester when distilled passes mainly into the  $\beta$ -ester. Dieckmann and von Auwers (*Ber.*, 1923, 56, 1527) regard the refractometric data for the fused material as confirming the structure (III), and Borsche and Thiele (*Ber.*, 1923, 56, 2132) find further confirmation in the fact that the catalytic hydrogenation of the  $\alpha$ -ester is more rapid than that of the  $\beta$ -ester.

This example of tautomerism is interesting in several respects.

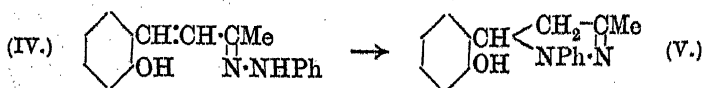
(1) The equilibrium can be studied either as a reversible or as an irreversible one.

(2) The  $\beta$ -form can be examined under conditions such that the enolic tautomeride is excluded.

(3) The relatively slow rate of change renders the course of the reactions amenable to spectrographic investigation.

In the preceding paper definite conclusions have been drawn concerning the absorption spectra of keto-enol tautomerides. The results of an examination of ring-chain tautomerides are now recorded. We are greatly indebted to Dr. A. McGookin of this University, who suggested and synthesised the compounds of this nature.

Spectrographic evidence shows that keto-enol tautomerides exhibit absorption maxima at the same wave-length but with differing absorptive power. In the cases of pure ring-chain tautomerism without elimination of water, *e.g.*,



(IV) shows two bands at 3600 Å. and 2545 Å. and (V) shows one band at 2790 Å. Ring-chain tautomerides thus differ markedly from keto-enol tautomerides in absorption spectra.

The dimeric modification of ethyl mesityloxidoxalate shows no selective absorption and the continuous absorption is relatively feeble, so that the presence of this form does not seriously interfere with the absorption of the  $\beta$ -form in various solvents.



The  $\beta$ -form in alcohol, hexane, or chloroform shows a well-defined band of high extinction coefficient, with  $\lambda$  (max.) varying a little for the different solvents. The enolic modification shows another band of high extinction coefficient, and a less noticeable shift due to the solvent. When a solution of the  $\alpha$ -form in any of the three solvents used was kept, the position of maximum absorption shifted towards the ultra-violet and the measured absorption curve was the sum of the curves due to the  $\alpha$ - and  $\beta$ -forms.

The  $\beta$ -form in presence of alkali shows three bands at  $\lambda$  (max.) 3512, 2867, and 2450–2500 Å. The first and the third are developed when alkali is added to the  $\alpha$ -(enolic) modification and are also shown by the pure sodium derivative. If alkali is added to the  $\beta$ -form, the system will contain unchanged  $\beta$ -ester and the sodium salt of the  $\alpha$ -ester. Hence the observed curve is a summation of two curves, one with a maximum at 2825 Å. due to the  $\beta$ -ester and the other with maxima at 3510 and 2457 Å., due to the sodium derivative of the  $\alpha$ -ester.

An alcoholic solution of the  $\beta$ -compound to which a large excess of sodium ethoxide had been added was left on ice. Later it was saturated with dry hydrogen chloride, and the sodium chloride filtered off. The solution then showed only one band, namely, the 3120 band due to the enolic ester.

The spectrographic data show that the reversible  $\alpha \rightleftharpoons \beta$  isomerism of ethyl mesityloxidoxalate resembles ring-chain tautomerism rather than keto-enol tautomerism. This conclusion is in agreement with the most recent chemical evidence. The metallic derivatives are probably co-ordinated compounds.

### Summary of Results.

Substance.	$\lambda$ (max.).	$\epsilon$ (max.).	$\lambda$ (min.).	$\epsilon$ (min.).
Ethyl $\beta$ -mesityloxidoxalate :				
Fresh solution in alcohol ...	2825	12,200	2275	3800
" " " hexane ...	2775	11,500	2310	3300
" " " chloroform	2850	11,500	2460	3700
Alcoholic solution plus 10	3512	13,000	3010	3700
equivs. of NaOEt .....	2867	7,500	2320	3400
	2495	7,500	—	—
Ethyl $\alpha$ -mesityloxidoxalate :				
Fresh solution in alcohol ...	3125	14,200	2415	3950
" " " hexane ...	3122	14,000	2420	3900
" " " chloroform	3125	15,100	2475	4750
Alcoholic solution plus 1	3510	16,500	2825	3500
equiv. of NaOEt .....	2457	6,750	—	—
10 equivs. " .....	3510	18,700	2825	3750
	2457	9,200	—	—
100 equivs. " .....	3510	21,250	2870	3800
	2457	9,200	—	—

*Ethyl Formylphenylacetate.*

Four forms of this substance have been recorded :

- (1) Liquid, b. p.  $135^{\circ}/15$  mm.; enolic.
- (2) Solid, m. p.  $70^{\circ}$ ; regarded as an aldo-form or as a geometrical isomeride of (3).
- (3) Solid, m. p.  $100-110^{\circ}$ .
- (4) Solid, m. p.  $50^{\circ}$  (Michael's modification).

Doubtless these forms are not all isomerides. Wolf (*J. Physical Chem.*, 1900, 4, 123) has shown that by keeping the ester at different temperatures for long periods it can be made to melt at any temperature between  $50^{\circ}$  and  $100^{\circ}$ , the former temperature being a stable triple point in the phase diagram. The difference in m. p. and refractivity of the various forms is due to one or more of the alternatives: (1) keto-enol tautomerism, (2) stereoisomerism, (3) unequal degrees of association. Michael and Fuller (*Annalen*, 1912, 391, 275) have adduced evidence that all the forms are unimolecular. The conclusion is drawn that only three forms exist having b. p.  $125^{\circ}/9$  mm., m. p.  $40^{\circ}$ , and m. p.  $100-103^{\circ}$ , respectively, all of which are enolic, since they react with aliphatic tertiary amines.

Wislicenus, however, after studying the isomerism of ethyl formylphenylacetate over a period of 30 years, draws the conclusion that the only two forms possessing real existence are ( $\alpha$ ), b. p.  $125-126^{\circ}/9$  mm., and ( $\beta$ ), m. p.  $103-105^{\circ}$ . All other "forms" he regards as mixtures of the  $\alpha$ - and the  $\beta$ -form. These he considers, after reviewing all the available evidence, to be *cis*- and *trans*-isomerides.

Together with his pupils he has studied the methyl formylphenylacetates and has found two modifications: ( $\alpha$ ), m. p.  $40-41^{\circ}$ , and ( $\beta$ ), m. p.  $91-93^{\circ}$ . No mixtures occur.

The  $\alpha$ -modification is undoubtedly enolic, but the  $\beta$ -form presents difficulties, since it is doubtful whether it exists as an aldo-form or as a geometrical isomeride of the  $\alpha$ -form. The two modifications react differently with copper acetate, and the  $\beta$ -form will under no conditions develop a coloration with ferric chloride. The anilides and piperidides of formylphenylacetic acid give two modifications, both of which are enolic. Michael considers that the aldo-modification has never been isolated and that much of the earlier work was misinterpreted owing to the fact that the  $\beta$ -form can add on a molecule of alcohol. For example, methyl formylphenylacetate-

methyl alcoholate is a crystalline substance, m. p. 89—92°, which does not develop a colour with ferric chloride.

Dieckmann (*Ber.*, 1917, 50, 1375) concludes that the ethyl ester exists in the pure state only as a liquid enol,  $\alpha$ , and a solid, m. p. 110°, which also is enolic.

Preparations of ethyl formylphenylacetate were examined having b. p. 127°/10 mm., m. p. 70°, and m. p. 100°, respectively. No maxima were found in the absorption curves, which were similar in extinction coefficient (order 7500 at 2600 Å.) and inflexions (2600—2100). With alkali, a definite band was obtained with a maximum at 2740 ( $e$  max. 19,200, 22,200, 16,800).

The interpretation of these results is somewhat difficult. Although ketones show well-defined maxima, in this substance the carbonyl group is a part of the formyl radical, so that the absence of the ketonic band does not prove the non-existence of an aldo-form. The data do not show the very large variations of  $e$  which are observed in keto-enol tautomerism. The absorptive powers of *cis*- and *trans*-isomerides (Errara and Henri, *Compt. rend.*, 1925, 181, 549) for a given wave-length are in the ratio 1 : 1—2, generally near 1.0—1.2. This is precisely the kind of variation observed in ethyl formylphenylacetate. Hence the spectrographic data strongly support the conclusion that the isomerism of this substance is of the *cis*- and *trans*-variety.

### *Ethyl Diacetylsuccinate.*

The isomerism of this ester has been the subject of much controversy. Two definite modifications were isolated and examined spectrographically :

Isomeride, m.p. 92°;  $\lambda$  (max.) = 2490,  $e$  (max.) 7600.

Isomeride, m. p. 31°;  $\lambda$  (max.) = 2490,  $e$  (max.) 6250.

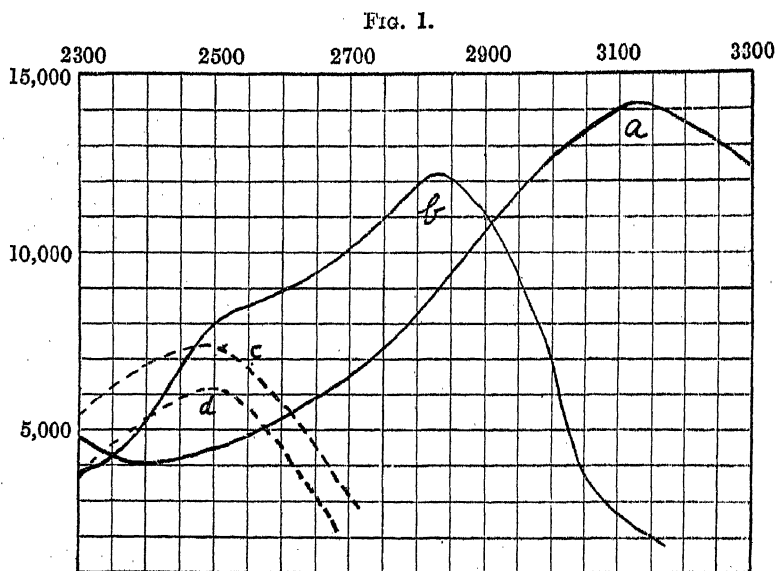
With alkali both forms exhibit a band at  $\lambda = 2750$  ( $e$  max. varying with the alkali/ester ratio).

The two substances provide an interesting comparison with ethyl acetoacetate :

	Acetoacetate.	Diacetylsuccinate.
Enol band .....	2430Å.; $e$ , 10,000	2490Å.; $e$ , 7600 6250
Keto band .....	2700Å. app.; $e$ order 100.	unknown.
Co-ordinated sodium salt	$\lambda$ (max.) 2725.	$\lambda$ (max.) 2750.
Ratio of extinctions .....	enol/keto = 100 : 1 (order)	m.p. 92°/m.p. 31° = 1.22.

The following results are from Henri and Errara's work. The

figures denote the ratio of  $\epsilon$  for the *trans*-isomeride to  $\epsilon$  for the *cis*-isomeride at the wave-lengths cited.



(a) Ethyl  $\alpha$ -mesityloxidoxalate in alcohol. (b) Ethyl  $\beta$ -mesityloxidoxalate in alcohol. (c) Ethyl diacetylsuccinate, *m. p.* 92°, in alcohol. (d) Ethyl diacetylsuccinate, *m. p.* 31°, in alcohol.

Substances.	$\lambda$ 2520Å.	$\lambda$ 2410Å.
CHCl:CHCl	1.4	2
CH <sub>2</sub> Et:CHBr	1.15	1.2
CHMe:CHBr	1.5	1.5
CHI:CHCl	1.3	1.25

Hence the data provide strong support for the view that the isomerism of ethyl diacetylsuccinate is of the *cis-trans* type.

One of us (E. R.) wishes to express his gratitude to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant. We are very grateful to Professor E. C. C. Baly, C.B.E., F.R.S., whose advice and encouragement have been of great value to us.

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XCIX.—*Absorption Spectra of Mesityl Oxide.*

By RICHARD ALAN MORTON.

HARRIES (*Ber.*, 1899, **32**, 1329; *Annalen*, 1904, **330**, 189) has stated that when mesityl oxide was shaken for 36 hours with a 40% solution of sodium bisulphite, 30% of the material remained unchanged. The residue obtained after shaking five times with fresh solutions of sodium bisulphite showed a refractive index and a density differing in the third decimal place from those of the original ketone. It appeared, nevertheless, to be mesityl oxide, since it yielded the same *cis*- and *trans*-oximes. Since the mesityl oxide regenerated from the bisulphite compound reacted completely with fresh sodium bisulphite, Harries concluded that the phenomena were not due to tautomeric equilibrium but to a new type of isomerism. Experiments were therefore made in order to determine whether the absorption spectrum of the inactive form differs from that of ordinary mesityl oxide.

Mesityl oxide synthesised from acetone by means of hydrogen chloride proved to be spectroscopically identical with the redistilled commercial material, b. p. 128°, which was used in an attempt to repeat the work of Harries. The results were as follow :

- (1) The whole of the mesityl oxide reacted with sodium bisulphite.
- (2) The yield of double compound was practically quantitative.
- (3) The ketone regenerated from the bisulphite compound was identical with the original product in respect of (a) boiling point, (b) absorption spectrum in the liquid state, (c) absorption spectrum in alcoholic solution.

(4) Earlier results (Henri and Bielecki, *Compt. rend.*, 1914, **158**, 567, 866, 1022; Purvis and McClelland, *J.*, 1913, **103**, 433) were confirmed.

(5) Four distinct absorption bands were found. Shifts due to solvent occurred, but none due to vapour-liquid, the pure liquid ketone showing the same frequency of maximum absorption as the vapour.

*Summary of Data.*

	$\lambda$ max. Å.	Present work.	Other work.
		$\epsilon$ max.	
Vapour .....	3239	low	Purvis and McClelland found $\lambda$ max. = 3238.
Liquid .....	3240	58	—
Alcoholic solution .....	3130	55	Henri and Bielecki found max. = 2380.
	2380	14,000	
Aqueous solution .....	2440	11,000	—
Hexane solution .....	3272	56	—
	2348	14,000	2335
Heptane solution .....	3275	50	—
	2330	14,000	—

It must be concluded that some unrecorded factor entered into the work of Harries.

I wish to express my thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for his interest and advice.

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C.—*Studies of Dynamic Isomerism. Part XXI. The Velocity of Mutarotation of Tetramethylglucose and of Tetra-acetylglucose in Aqueous Acetone.*

By GRIFFITH GLYN JONES and THOMAS MARTIN LOWRY.

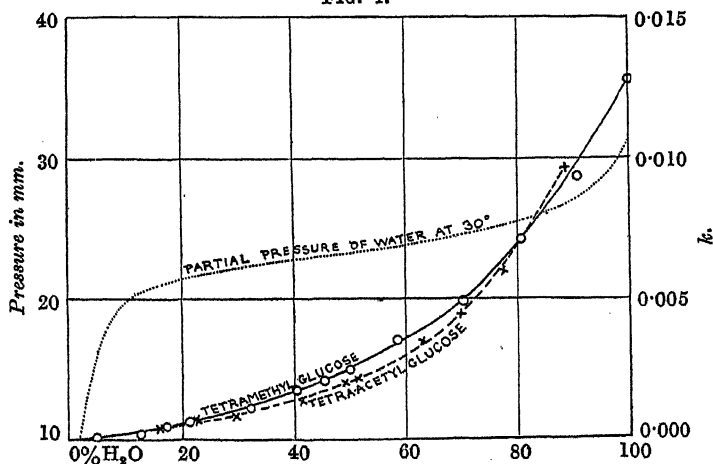
ALTHOUGH it has long been known that water is an effective catalyst for the mutarotation of the sugars, even apart from the presence of basic or acidic impurities (see Part I, J., 1903, **83**, 1314), there was until recently no clear picture available as to the way in which the water intervenes in order to determine the changes of structure which give rise to the observed changes of rotatory power. In particular, although it was known that the formation of a hydrate does not bring about any marked alteration of the rotatory power of  $\alpha$ -glucose, and cannot therefore be a direct cause of the mutarotation of this sugar (Part III, J., 1904, **85**, 1551), there were no experimental data to show how the subsequent molecular rearrangement of the hydrate was effected. It was suggested, however, in a recent paper (Part XVIII, J., 1925, **127**, 1371) that there is a marked analogy between the conditions under which mutarotation occurs and those which are used to promote the hydrolysis of an ester, and that, since mixtures of acids and bases with water are even more efficient catalysts than water itself, the action of the water probably depends on its amphoteric properties. If this view were correct, any solvent which can accept a proton from the sugar, and return it to the sugar residue, might act as a complete catalyst for the mutarotation. This conclusion has been verified (Part XX, J., 1925, **127**, 2883) by the discovery that an anhydrous mixture of pyridine and cresol is an excellent catalyst for the mutarotation of tetramethylglucose.

The experiments now described were undertaken in order to secure information in reference to solvents which appear to diminish the catalytic activity of water instead of increasing it. The choice of acetone as a diluent was dictated by the fact that Irvine (J., 1913, **103**, 584) has found it to be a particularly easy solvent in which to effect an arrest of mutarotation in a methylated sugar. It was thought that this might be due to some restraining action of the

acetone upon the water or upon the other impurities which give rise to mutarotation in inert solvents. We therefore anticipated that, when mixed with water in various proportions, acetone would reduce the catalytic activity of the water more rapidly than its total concentration. The results recorded in Tables I and II show that this anticipation was amply fulfilled. Thus in a 50% mixture of acetone and water the velocity of mutarotation of tetramethylglucose is only about 20% of that in pure water. The water in this solution has therefore less than one-half of its normal activity in the free state.

We have also compared the velocity coefficients in Tables I and II with the partial vapour pressures of aqueous acetone at 30° as recorded by Makovetzki (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 226),

FIG. 1.



but can find no indication of any parallelism between them. In particular, the velocities shown in the figure appear to rise progressively from the origin at 0%  $\text{H}_2\text{O}$ , where the curves are perhaps tangential to the horizontal axis, whilst the dotted curve which shows the partial vapour pressure of water is inflected in the normal fashion for mixtures showing strong positive deviations from Raoult's law of lowering of vapour pressure. We therefore conclude that the catalytic activity of the water, which is obviously not proportional to its total concentration, is also not a simple linear function of its activity as measured by its partial vapour pressure above the solution.

#### EXPERIMENTAL.

The physical constants of the tetramethylglucose used in these experiments have already been given (*J.*, 1925, 127, 1387, footnote);

they are in close agreement with those recorded by Irvine. The purity of the sample is, however, guaranteed even more effectively by the arrest of mutarotation observed in several inert solvents; moreover, the mutarotation constants of the sugar were not altered appreciably by three further crystallisations from ether and from petrol:

	Initial.	Specific rotation, $[\alpha]_{5461}$ .		Vel. coeff.
		Final.	Ratio.	
Before recrystallisation .....	117°	95°	1.23	0.0128
After                    " .....	115	94	1.23	0.0124

The tetra-acetylglucose was prepared for us by Messrs. Boots Pure Drug Co., Nottingham, to whom we wish to express our thanks for their generous gift. The substantial purity of the specimen was established by analysis, but we have not been able to find any trustworthy figures for the physical constants of the compound. The melting point, 118°, given by Fischer and Delbrück (*Ber.*, 1909, 42, 2779) has no clear significance, since prototropic compounds have two different melting points, according as time is allowed for isomeric change to take place or not. In the case of tetra-acetylglucose we find that the true melting point, at which the compound melts in about 10 seconds when plunged into a bath heated to a known temperature, is 123°, as recorded by a standardised Anschütz thermometer graduated to 0.2°; and that the "equilibrium temperature" (Lowry, J., 1899, 75, 233), at which the compound melts or re-melts when heated slowly, is 110°. Since a small specimen of tetra-acetylglucose given to us by Professor Haworth melted at the same temperatures, within less than a degree in each case, we feel justified in putting forward these temperatures as provisional standards, which can be verified by comparison with values recorded in the future for other specimens of the purified sugar. The rotatory powers given by Fischer and Delbrück,  $[\alpha]_D^{20} = +2.19^\circ$  to  $+82.7^\circ$ , were apparently determined at room temperature, with unpurified sodium light, and in alcohol of unspecified water content. We have not attempted to make any exact comparison with these uncertain data, but in our opinion the value  $[\alpha]_{5461} = +6^\circ$  for a 5% solution of tetra-acetylglucose in pure anhydrous acetone at 20° can be accepted provisionally as a characteristic constant of the unchanged sugar, since this value is permanent over a period of several hours. As in the case of tetramethylglucose, the purity of the sample used in our experiments was established most satisfactorily by the complete arrest of mutarotation which we have observed repeatedly in solutions of the sugar in an inert solvent. Since the suggestion has been made that the mutarotation of tetra-acetylglucose in aqueous acetone may be due in part to hydrolysis instead of to isomeric change, we have made direct experiments to test this point, but could



not detect any hydrolysis after a week at a temperature of about  $18^{\circ}$ ; after 10 days, the proportion of sugar hydrolysed was only of the order of 0.5%. After 7 months, the residues from the original experiments were hydrolysed to the extent of only 5%. The hydrolysis of the sugar can therefore have had no perceptible influence on the velocity of mutarotation, a conclusion which we had already anticipated from the steadiness of the observed end-points, since it was incredible that hydrolysis (as well as isomeric change) could be complete in the course of a few hours or days.

The acetone had been purified through the compound with sodium iodide (J., 1913, 103, 1255). The solutions were prepared by dissolving about 1 g. of tetramethylglucose, or 0.5 g. of tetra-acetylglucose, in 20 c.c. of an aqueous acetone made up by weighing. Tetramethylglucose was examined over the whole range of concentrations from 0 to 95% of acetone, but tetra-acetylglucose is almost insoluble in water and only slightly soluble in water containing 5% of acetone. A solution of the latter concentration was prepared by dissolving the sugar in acetone and adding the necessary quantity of water; but the constants of the mutarotation curve were unsatisfactory, and the values for this solution have not been included in the table. The very slow mutarotations in acetone containing only traces of water were not included in the present research. In order to economise space, all the individual readings have been omitted, but the unimolecular velocity coefficients for the various solutions are set out in Tables I and II, and are shown graphically in the figure.

TABLE I.

Mutarotation of Tetramethylglucose in Aqueous Acetone at  $20^{\circ}$ .

Acetone %.	Acetone, mols. %.	$k \times 10^5$ .
0	0	1280
9.25	3.08	934
19.20	6.9	710
29.7	11.8	487
41.4	18.0	351
50.0	23.7	246
54.6	27.3	206
59.6	31.4	177
67.7	39.4	110
78.7	53.4	60
82.8	59.5	45
87.3	69.8	18.4
95.1	85.7	3.0

TABLE II.

Mutarotation of Tetra-acetylglucose in Aqueous Acetone at  $20^{\circ}$ .

Acetone %.	Acetone, mols. %.	$k \times 10^5$ .
11.5	3.7	985
22.6	8.0	596
30.0	11.6	441
36.8	15.0	346
48.4	23.5	217
50.7	24.6	200
58.5	30.6	129
70.3	42.1	80
77.3	50.7	60
83.9	61.8	28

## CI.—*Absorption Spectra of Condensed Nuclear Hydrocarbons.*

By NORMAN STEWART CAPPER and JOSEPH KENNETH MARSH.

It was shown recently that visible absorption bands attributed to anthracene were due to an impurity, chrysogen (*J. Amer. Chem. Soc.*, 1925, 47, 2847). It has now been found that other coal-tar hydrocarbons have been insufficiently purified for spectroscopic examination. Thus the four chief hydrocarbons boiling between 275° and 360° cannot be separated by crystallisation, as they appear to form mixed crystals. In particular, fluorene and phenanthrene retain traces of anthracene, which can be detected by its intense ultra-violet absorption. The absorption bands of the purified substances exhibit constant frequency differences, which have been attributed to the double carbon bond in the aromatic series (Marsh, *Phil. Mag.*, 1925, 49, 971, 1206). Other synthetic hydrocarbons also have been examined.

*Purification of Phenanthrene and Fluorene from Anthracene.*—A good commercial phenanthrene showed anthracene bands of an intensity corresponding with a content of about 16%, and this was not greatly reduced by fractional crystallisation. The melting point gives no trustworthy information as to the purity. In the fluorene used, the anthracene content was not more than 1 or 2%.

Purification of both substances was effected by refluxing a strong xylene solution by the heat from a silica mercury vapour lamp. The light caused the anthracene present to polymerise, even in glass vessels. Owing to its very slight solubility, the dianthracene produced was readily separated, but since anthracene and dianthracene attain to an equilibrium repeated light treatments and separations were necessary. About 1% of anthracene was thus eliminated from Kahlbaum's "purest reagent" phenanthrene. The spectra of the purified products examined in concentrated chloroform solutions indicated an anthracene content of about 0.01% in the phenanthrene and 0.001% in the fluorene. The melting point of the fluorene was 114–114.5°, a value higher than that commonly accepted. The phenanthrene melted at 98°. The higher values usually quoted probably result from the eutectic mixture with anthracene containing very nearly 100% of phenanthrene. The purified material in both cases lost its visible fluorescence, even in strong actinic light, or in the case of phenanthrene at most only a slight trace remained.

The absorption spectra were studied with a Hilger spectrophotometer and condensed copper spark. Little description will be

necessary if the absorption curves, the photographic reproductions, and the table of band positions are examined.

*Phenanthrene*.—Previous spectroscopists have used specimens containing from 0.3% (Baly and Tuck, J., 1908, 93, 1902) to upwards of 10% of anthracene, masking completely the true spectrum, which in the region above 3000 Å. is some 25 times weaker than that of anthracene. Probably the small narrow band recorded at about  $1/\lambda 4000$  is due to the remaining trace of anthracene, and a very faint band at  $1/\lambda 3120$  to acenaphthene.

*Fluorene*.—A band found at  $1/\lambda 3117$  may be ascribable to the presence of 1% of acenaphthene.

*Anthracene, 9-phenylanthracene, and 1:2-benzanthracene* have very similar spectra. Relatively to those of anthracene, 9-phenylanthracene has its bands shifted about 60 units towards the visible spectrum, and they are not so distinct. In 1:2-benzanthracene, the weaker member of each pair appears on the red side of the strong band, but the first pair is very weak. In the middle ultra-violet, bands corresponding to those found in phenanthrene are seen. The structure may be regarded as 2:3-benzphenanthrene.

On examining anthracene vapour (20 cm.) at 50° to 120°, both of the strongest bands were seen to have a weak neighbour on each side, and there was also a faint band midway between the two strong ones. The bands were shifted almost 100 units with respect to their solution positions.

*Octahydroanthracene* lacks entirely the set of bands above  $\lambda 3000$  found in anthracene, but has several at about  $1/\lambda 3500$  to 3700, i.e., in the same region as those in other alkyl derivatives of benzene.

*Bisdiphenylene-ethylene*,  $(C_6H_4)_2C:C(C_6H_4)_2$ , showed only a broad band in the blue region, an undeveloped one at about  $1/\lambda 3600$ , and another at about 4100.

*Chrysogen*.—This substance of unknown structure occurring in small quantities—probably less than 0.1%—in most samples of anthracene has an anthracene nucleus, since it is capable of polymerising similarly to anthracene itself. Its spectrum is distinctly of the polynuclear hydrocarbon type. In fused anthracene the band positions are 60–80 Å. nearer the red end of the spectrum.

*Other Polynuclear Hydrocarbons*.—In the substances examined, except fluorene and octahydroanthracene, every carbon atom has an unsatisfied valency, and except for bisdiphenylene-ethylene the unsaturation is entirely aromatic in character. Leaving aside these three, the chief feature of the spectra is a series of rather narrow bands between  $\lambda 3000$  and 4000, which show a constant frequency difference of about 142 waves/mm. Previous workers have examined other hydrocarbons which come into the same

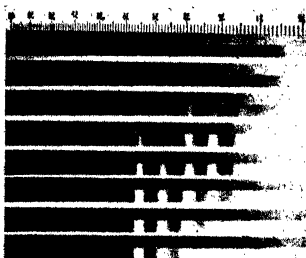
category. These substances also exhibit narrow bands, although the interval may vary. The absorption bands of benzene vapour are spaced 92.4 units apart (Henri, *J. Phys. Radium*, 1922, 3, 181) and the emission bands at 98.7 unit intervals (J., 1923, 123, 642). Naphthalene vapour shows a long series of bands, both absorption (Henri and László, *Proc. Roy. Soc.*, 1924, A, 105, 662) and emission (Dickson, *Z. wiss. Photochem.*, 1912, 10, 166), at 47.4 unit intervals. The emission spectrum shows every third band stronger than its neighbours, making an interval of 142 as in anthracene, etc. Baly and Tuck found in chrysene (J., 1908, 93, 1902) four bands as nearly as can be determined at 140 unit intervals. A partial examination of picene, 2:3:6:7-dibenzanthracene, and  $\beta\beta$ -dinaphthyl was made by Homer and Purvis (J., 1908, 93, 1319).

## TABLE OF BANDS.

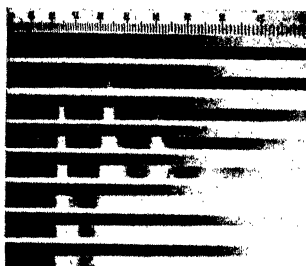
The figures are oscillation frequencies, and in italics are the frequency intervals. Small bands detected but difficult to locate accurately have been omitted.

Anthracene.	2661	2701 <i>143</i>	2804	2844 <i>143</i>	2947	2994 <i>143</i>	3090
	3133 <i>141</i>	3231 <i>98</i>	3231 <i>103</i>	3373 <i>142</i>	3960 <i>6 \times 98</i>	4058 <i>98</i>	96
Vapour.	2725	2759	2797	2830	2864	2899	2934
	(2759 and 2899 correspond to solution bands 2666 and 2804.)						
Phenanthrene.		2895	2958 <i>138</i>	3033	3100 <i>138</i>	3171	3243 <i>140</i>
		3415 <i>140</i>	3555 <i>99</i>	3654	3787 <i>2 \times 101</i>	3990 <i>142</i>	4132
9-Phenylanthracene.	2603	2743 <i>140</i>	2883 <i>140</i>	2883 <i>141</i>	3024	3917	
1:2-Benzanthracene.	2599	2670 <i>140</i>	2740	2787	2826 <i>143</i>		
	2930	3070 <i>140</i>	3339	3479 <i>140</i>			
Chrysogen.	2105	2247 <i>142</i>	2389 <i>142</i>				
Fluorene.	3117?	3333	3426	3820			
Octahydroanthracene.	3268	3333	3506	3580	3629	3686	
Bisdiphenylene-ethylene.	2190	3610	4130	(All broad and indefinite)			

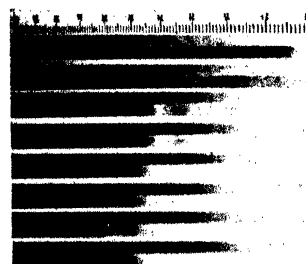
Benzene and the other eight condensed nuclear hydrocarbons all have the same type of multiple narrow-banded spectra, the main intervals being generally 142 units in the heavier molecules, 142 or 142/3 in naphthalene, and  $142 \times \frac{2}{3}$  in benzene. The simple methyl and other derivatives may also give spectra consisting of



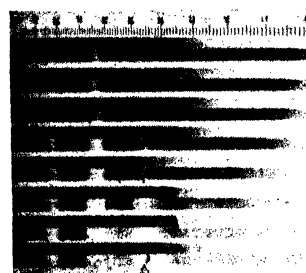
Phenanthrene. 1 cm.  $M/200$ .



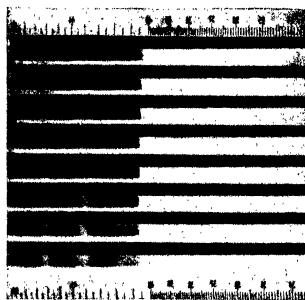
Anthracene. 1 cm.  $M/5000$ .



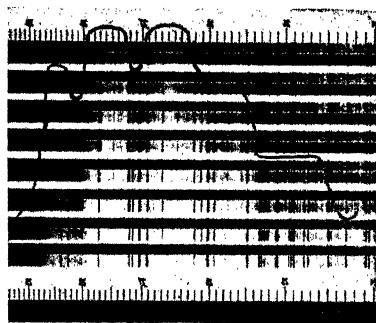
1:2-Benzanthracene.  
1 cm.  $M/5000$ .



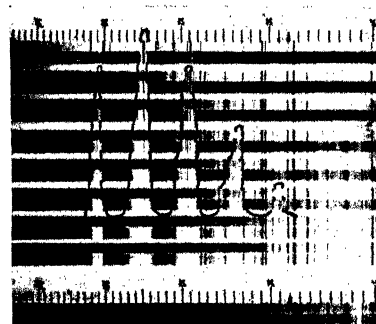
9-Phenylanthracene.  
1 cm.  $M/5000$ .



Chrysogen in 4 cm. of  
 $M/10$ -anthracene.



Naphthalene. 1 cm.  $M/5000$ .

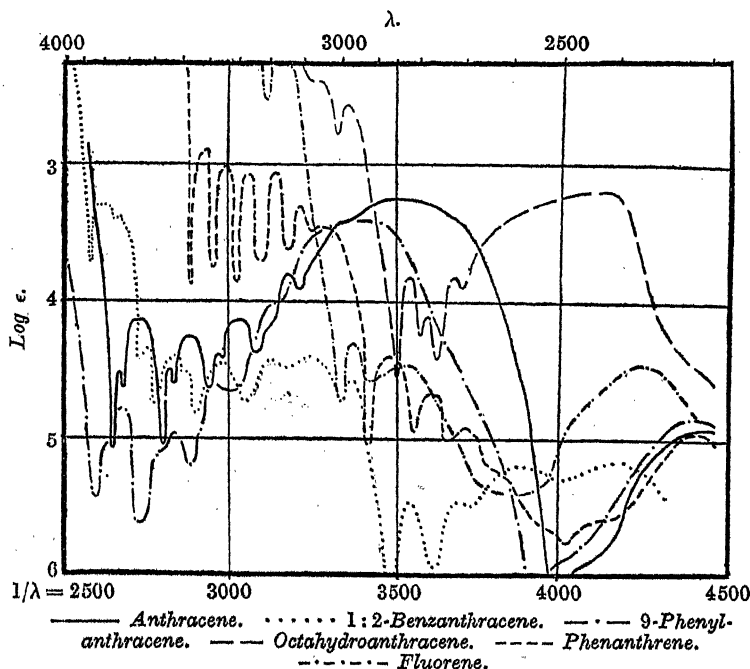


Benzene. 1 cm.  $M/200$ .



a number of narrow bands, but the regularity and sharpness are usually less marked, *e.g.*, László (*Z. physikal. Chem.*, 1925, **118**, 369) finds band series at the intervals 154, 142.5, 147, and 138, for 1-methyl-, 2-methyl-, 2:7-dimethyl-, and 2:6-dimethylnaphthalene, respectively. In phenanthrene alternate bands are similar and show the interval 142, the intermediate ones being not quite centrally situated.

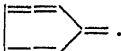
FIG. 1.



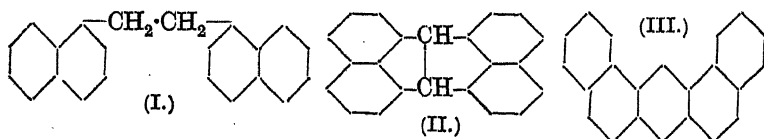
Besides the series of five or six bands already mentioned, most of the substances give other bands farther in the ultra-violet and of greater intensity. There is usually one well marked, with, on the more refrangible side, other less distinct bands, again at intervals of 142 units. Phenanthrene and 2:3-benzphenanthrene (1:2-benzanthracene) have also a third intermediate region.

#### Discussion of Results.

By removing all anthracene from phenanthrene and fluorene, entirely new absorption curves for these two substances have been found. Fluorene now gives a spectrum similar to that of *o*-xylene or other simple substituted benzene derivative. Phen-

anthrene presents a spectrum differing from that of anthracene in strength, band position, and arrangement. Hyatt (*Physical Rev.*, 1922, 19, 391), employing the same methods as ours, measured 16 bands for anthracene. Three of these not now observed were possibly due to phenanthrene. We do not find that the remainder can be divided into a series at intervals of 147 and another at 142. Both our series run at intervals of 142. The spectral type of bisdiphenylene-ethylene differs completely from that of the other polynuclear hydrocarbons. The strong red colour is associated with the ethylenic bond, disappearing on its reduction, and it constitutes with its neighbours the characteristic system of the visibly coloured fulvenes, .

The spectrum of stilbene, the simplest example of a substance containing an ethylenic bond between benzene nuclei, consists of a single broad band at about  $\lambda 3300$ : in phenanthrene this double bond becomes aromatic, and half-a-dozen narrow bands occupy the same region. Thus the effect of an ethylenic bond is to cause the fusion of the aromatic bands. Another substance having an absorption curve very similar to those of bisdiphenylene-ethylene and stilbene and in a position intermediate between them was examined by Purvis and Homer (J., 1909, 97, 1155). It was a product of the reaction between tetrabromoethane and naphthalene. They concluded, largely on spectroscopic evidence, that it was 1:2:7:8-dibenzanthracene. Its spectrum, however, is entirely different from what we have found for 1:2-benzanthracene and would be the only deviation from the type characteristic of the class of substances to which their formula would relegate it. Ethylene dibromide and naphthalene were considered to give rise to *s*-di- $\alpha$ -naphthylethane (I), which then broke down to picene. Tetrabromoethane and naphthalene might therefore give rise to the substance (II), and this would be much more likely to give a spectrum with broad bands than would a substance having the suggested formula (III).



*Relationship to Infra-red Spectra.*—It does not seem possible to offer any detailed explanation of the differences which make all these closely related spectra individually characteristic, but the cause of the similarity constituting the spectral type found in this



group of hydrocarbons must be some common factor, and therefore one or more of the following: (a) a benzene ring, (b) a  $C \equiv C$  linking, (c) a  $CH$  group. These possibilities will be considered with reference to the known features of the infra-red spectra of these or similar substances. Coblenz (*Carnegie Inst. Publication*, No. 35, 1905), from a study of some thirty hydrocarbons, concluded that characteristic absorption maxima due to methyl and methylene groups are found at 3.43, 6.86, 13.6—13.8, and 14  $\mu$ . Weniger (*Physical Rev.*, 1910, **31**, 388) gives also a band at 7.3  $\mu$ . In the aromatic series, Coblenz gives the following bands as characteristic of benzene: 3.25, 6.75, 8.68, 9.8, 11.8, and 12.95  $\mu$ . The first two and the last are identifiable with bands in hydrocarbons of the aliphatic series, but, owing to the unsaturation of the carbon atom of the  $CH$  group, their frequency is increased somewhat. Thus the 3  $\mu$  band has the value 3.08 for acetylene, 3.25 for benzene, 3.28 for ethylene, and 3.39 for ethane.

The strongest bands of ethylene are:

$\lambda$ .....	(21)	10.5	6.98	5.3	3.28
$1/\lambda$ .....	(47.6)	95.24	143.3	188.9	304.9
Diff. ....		47.6	48.1	45.6	—

Except the last, these are evidently multiples of a band which should occur at  $1/\lambda 47.6$ , and may be considered as due to  $C:C$ . In benzene vapour, is a series of bands at intervals of 15.9, *i.e.*, 47.6/3; in naphthalene, the series interval is 47.4 and in the heavier hydrocarbons 142, *i.e.*,  $47.4 \times 3$ . The ethylene band 6.98  $\mu$  occupies also the position of a  $CH$ -band. The fifteen aliphatic hydrocarbons examined by Coblenz show, as consistently the most prominent in their spectrum, two bands at about 6.86 and 7.33  $\mu$ . The frequencies (145.8—136.4 waves/mm.) are just what are found to be the intervals between the ultra-violet bands of the polynuclear hydrocarbons. Experimental difficulties have prevented thorough investigation of the infra-red spectra of the solid aromatic hydrocarbons. Stang (*Physical Rev.*, 1917, **9**, 342), however, has examined naphthalene and several of its derivatives and finds a band at 7.19  $\mu$  ( $1/\lambda 139.1$ ) to be among the strongest in the spectrum. It remains therefore an open question as to whether this common frequency difference is due to  $CH$  or  $C:C$ , but probably it is a frequency to which both can resonate and for this cause it dominates the infra-red and ultra-violet spectra. Indeed, if any sort of harmonic motion is to be preserved in the molecule, it is necessary that different oscillations should be in tune with one another, and that the relative frequencies must be expressible as whole numbers.

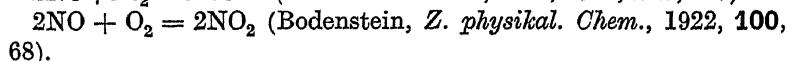
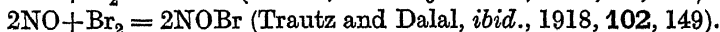
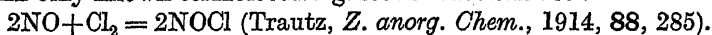
We are much indebted to Mr. E. de B. Barnett for supplying very pure samples of the three anthracene derivatives examined.

THE SIR DONALD CURRIE LABORATORIES, QUEEN'S UNIVERSITY,  
BELFAST, NORTHERN IRELAND. [Received, December 5th, 1925.]

## CII.—*The Interaction of Nitric Oxide and Hydrogen and the Molecular Statistics of Termolecular Gaseous Reactions.*

By CYRIL NORMAN HINSHELWOOD and THOMAS EDWARD GREEN.

THE only known termolecular gaseous reactions are :



We have succeeded in measuring a homogeneous change between nitric oxide and hydrogen in the region of 1100° Abs., which proceeds in accordance with the equation

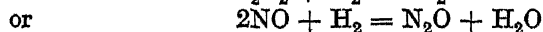
$$-d[\text{NO}]/dt = k[\text{NO}]^2[\text{H}_2] \quad . \quad . \quad . \quad (1)$$

and is thus termolecular.

The ultimate result of the interaction being expressed by the equation



it must be supposed that the action takes place in stages thus,



the second stage in either of the alternatives being a rapid reaction subsequent to the main change of which the speed is measured.

There are reasons why this new reaction possesses considerable interest. These may be briefly outlined as follows.

The majority of known gaseous reactions are bimolecular. The application of the kinetic theory of gases leads to a simple explanation of these. The molecules which react are those which collide while they possess the "energy of activation," which can be found from the temperature coefficient of the reaction velocity. When the total number of collisions taking place in unit time is multiplied by  $e^{-E/RT}$ , a fraction representing the chance that the energy of the colliding molecules shall exceed the energy of activation,  $E$ , a number is obtained which is very nearly equal to the number of

molecules which actually undergo chemical transformation. Thus the possession of the energy of activation seems to be the only important factor in bimolecular reactions. Since the number of collisions depends on the molecular diameter, and since all molecular diameters are of the same order,  $10^{-8}$  cm., the rate of a bimolecular change is chiefly determined by the value of  $e^{-E/RT}$ . We find, therefore, that different bimolecular reactions attain approximately equal rates at temperatures which make  $E/RT$  respectively the same for each (Hinshelwood and Hughes, J., 1924, 125, 1841; Hinshelwood and Thornton, *Phil. Mag.*, 1925, 50, 1135).

A bimolecular gaseous reaction which takes place with conveniently measurable velocity in the neighbourhood of  $350^{\circ}$  Abs. will have a heat of activation of about 20,000 calories, at  $700^{\circ}$  Abs. about 40,000 calories, and one which attains an equal speed at  $1000^{\circ}$  Abs. will have a value of about 60,000 calories. No exception is known to this rule, so that if we know the rate of a bimolecular reaction at a given temperature we can form a fairly accurate estimate of the heat of activation.

From the point of view of the molecular statistics of chemical change termolecular reactions are of special interest, since they depend on the rather rare event of a collision between three molecules. Bodenstein estimates the frequency of termolecular collisions to bear about the same proportion to the frequency of bimolecular collisions as the molecular diameter bears to the mean free path. At atmospheric pressure, the mean free path is of the order  $10^{-5}$  cm., and since the molecular diameter is of the order  $10^{-8}$ , ternary collisions should be about 1000 times less frequent than binary collisions. Thus if we have a bimolecular reaction and a termolecular reaction with equal heats of activation, the rate of the termolecular reaction should be at least 1000 times smaller than that of the bimolecular reaction at the same temperature. It will probably be more than 1000 times slower, since a considerable number of the ternary collisions are likely to be ineffective simply on account of unfavourable orientation of the molecules during impact. Taking this into consideration, it appears that the factor may be nearer 10,000.

Conversely, if a termolecular reaction and a bimolecular reaction were to take place at equal rates at the same temperature, then the heat of activation of the termolecular reaction would need to be the smaller by an amount  $\Delta E$ , such that  $e^{\Delta E/RT} = 1000$  to 10,000. Thus, other things being equal, the heats of activation of termolecular reactions ought to be about 5000 calories less at the ordinary temperature and about 15,000 calories less at  $1000^{\circ}$  Abs. than those of bimolecular reactions.

A bimolecular reaction which would take place at a rapid but measurable rate at the ordinary temperature would have a heat of activation of 12,000 to 15,000 calories, a termolecular reaction might therefore be expected to have one of 5000 to 10,000 calories. This would mean a very small temperature coefficient. Another factor enters, however, in this case, for Bodenstein found that the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ , instead of having a small positive temperature coefficient, had actually a very small negative temperature coefficient. This he attributed to the diminished "duration of collisions" at higher temperatures, which decreases the chance that two molecules shall still be within molecular distance of each other when a third approaches to complete a ternary collision. This factor is enough just to invert the small positive temperature coefficient which would otherwise be found. The other two termolecular reactions have in fact very small positive temperature coefficients. This new factor, therefore, is equivalent to the reduction of the apparent heat of activation by 5000 calories or so.

Trautz has an alternative explanation of Bodenstein's result. The reaction is supposed to be a bimolecular one between  $\text{N}_2\text{O}_2$  and  $\text{O}_2$ . But since  $[\text{N}_2\text{O}_2]$  is proportional to  $[\text{NO}]^2$ , the reaction is kinetically termolecular. The negative temperature coefficient is due to the increasing dissociation of  $\text{N}_2\text{O}_2$  at higher temperatures. The apparent heat of activation would thus be equal to the difference between that of the bimolecular reaction between  $\text{N}_2\text{O}_2$  and  $\text{O}_2$  and the heat of dissociation of  $\text{N}_2\text{O}_2$ ; and actually this difference comes out to be a small negative quantity.

Whichever way of regarding the matter is preferred—and there is not really much difference between the transitory existence of  $\text{N}_2\text{O}_2$  and a collision of finite duration between two molecules of NO—it is clearly of interest to examine the behaviour of a termolecular reaction which takes place at a much higher temperature, say in the neighbourhood of  $1000^\circ \text{Abs}$ . A bimolecular reaction which proceeded at a conveniently measurable speed at this temperature would have a heat of activation of approximately 60,000 calories. A termolecular reaction should therefore have one about 20,000 calories less.

The predicted heat of activation is thus about 40,000 calories. We find actually the heat of activation of the termolecular reaction between nitric oxide and hydrogen to be 44,000 calories. This result seems to show that termolecular reactions can be interpreted satisfactorily in terms of the simple kinetic theory, and to provide further evidence that the energy of activation is a quantity with a real physical meaning.

It is perhaps significant that the four termolecular reactions now

known all involve the participation of two molecules of nitric oxide. It may be simply coincidence, or it may be that the "duration of collision" is greater in encounters between molecules of nitric oxide than in encounters between other molecules, so that there is more chance of the third molecule arriving in time. Some may prefer to call this phenomenon, assuming it to be a real one, formation of  $N_2O_2$ .

*Preparation of the Gases.*—The hydrogen used was electrolytic and was purified from oxygen by passage over a hot platinum wire; it was then dried with phosphoric oxide. The nitric oxide was prepared in a state of purity by the "nitrometer" reaction and stored in contact with concentrated sulphuric acid in the vessel in which it was made.

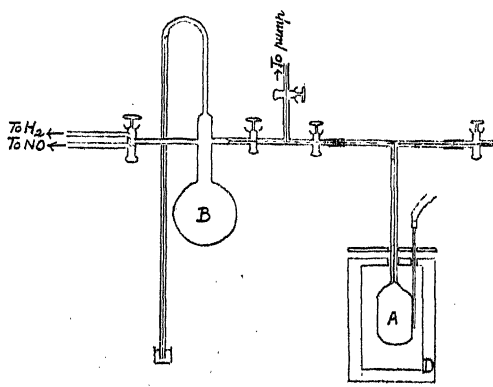
*Apparatus and Method of Measurement.*—Since the reaction is attended by a decrease in pressure, a simple manometric method can be employed. It is necessary, however, to prevent the condensation of the steam which is produced. This was done in the following way. The reaction vessels were of clear fused silica, 260 c.c. and 155 c.c. in capacity, respectively. The bulb was sealed to a long T-piece of fine silica capillary tube, which communicated with the manometer. The whole of this T-piece was heated to about  $140^\circ$ . Under these conditions, when the reaction took place in the heated bulb, no water vapour diffused through the length of capillary tube and condensed in the cooler part of the apparatus such as the capillary of the manometer itself. The silica capillary tube was joined to the glass parts of the apparatus by means of stout rubber joints. It was arranged that the silica and the glass made good contact beneath the joints, and careful observation showed that no disturbance of any kind arose from the presence of these. They were quite cold. The escape of hydrogen through the walls of the silica bulb at the temperature of the experiments was known from independent experiments to be negligible.

The arrangement of the apparatus is obvious from Fig. 1. *A* is the reaction bulb, heated in an electric furnace, the temperature of which was controlled by a thermo-couple and kept constant to about a degree by hand regulation of the heating current. The thermo-couple was standardised as described in previous papers (J., 1924, 125, 393). *B* is a reservoir in which the gases could be mixed before being allowed to stream into the reaction vessel. In some of the experiments it was omitted.

It was ascertained by direct experiment that the reaction tended asymptotically to the theoretical "end-point" and that diffusion of water vapour from the heated region did not occur during the time of an ordinary experiment.

*Kinetics of the Reaction.*—The main series of experiments were made at  $826^{\circ}\text{C}$ . This approaches the highest temperature at which experiments can be made accurately. The conclusions drawn about the nature of the reaction are as follows. It is almost entirely homogeneous at higher pressures, and is of the third order, its rate being proportional to the square of the pressure of the nitric oxide and to the first power of that of the hydrogen. At lower pressures, where the reaction is slower, it is less exactly of the third order, and, moreover, the straight line obtained by plotting the initial rate of reaction against the pressure of hydrogen does not pass exactly through the origin. These facts indicate that a certain amount of heterogeneous reaction takes place concurrently with

FIG. 1.



the homogeneous reaction. The heterogeneous change, as would be expected from the strong adsorption of hydrogen by silica, is probably almost independent of the hydrogen pressure. This assumption would explain also the failure of the reaction to follow the equation of a third-order reaction exactly at the lower pressures. These conclusions are confirmed by the addition of powdered silica to the reaction vessel to test for the existence of a surface reaction. There was found to be some, but it accounted for a small fraction only of the total change.

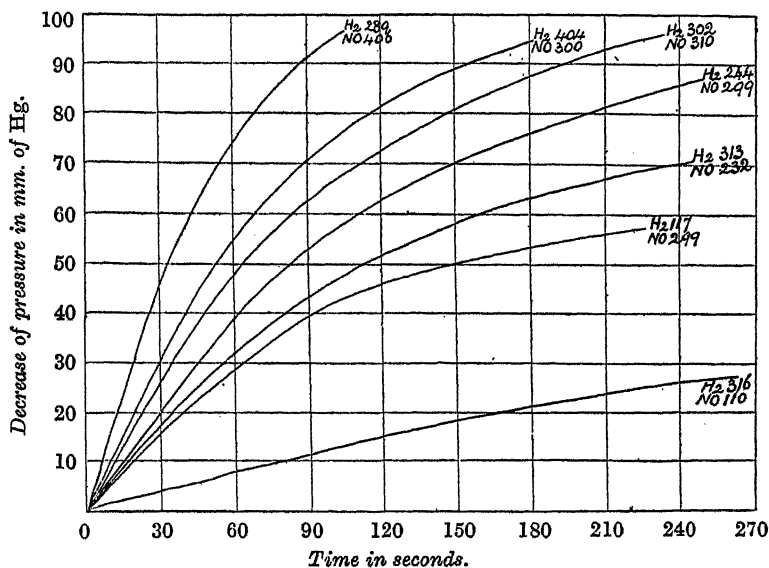
The results were very satisfactorily reproducible. For example, experiments 4, 5, and 31 of the whole series, which were made with the same pressures of nitric oxide and hydrogen, respectively, gave almost exactly superposable curves. This is in pleasing contrast with what is found when the reaction is one which takes place on the surface of the silica. A typical experiment is recorded below and others are shown in the curves of Fig. 2.

Temp. 826°. Initial pressure of NO = 406 mm. Initial pressure of  $H_2$  = 289 mm.,  $t$  is the time in seconds, and  $x$  the change of pressure in mm.

$t$ .....	8	13	19	26	33	43	54	69	87	110	140	204	310	$\infty$
$x$ .....	10	20	30	40	50	60	70	80	90	100	110	120	127	144.5

*The Order of the Reaction.*—The following experiments were made with equimolecular amounts of nitric oxide and hydrogen.  $\tau$  is the time in seconds required for half the reaction to complete itself,

FIG. 2.



Interaction of nitric oxide and hydrogen at 826° C.

Since the rate of reaction depends upon the square of the NO concentration but the first power only of the  $H_2$  concentration, a high pressure of nitric oxide has much more effect than a high pressure of hydrogen.

$a$  is the initial pressure in mm. of each gas, and  $n$  is the reaction order calculated from the equation  $(a_1/a_2)^{n-1} = \tau_2/\tau_1$ .

$a_1$ .	$\tau_1$ .	$a_2$ .	$\tau_2$ .	$n$ .
354	81	202	224	2.81
340.5	102	288	140	2.89
340.5	102	243	176	2.62
375	95	251	180	2.60

The reason why  $n$  falls a little under 3.0 will be discussed below.

*Influence of the Pressure of the Separate Gases.*—(a) *Nitric oxide.* Experiments were made in which a fixed initial pressure of hydrogen was used and various initial pressures of nitric oxide. Curves were plotted on a large scale and the initial rate of reaction was found by drawing tangents. The following figures show that the rate is

proportional to the square of the nitric oxide concentration. The initial pressure of hydrogen was 400 mm. in each instance.

[NO]. (mm.).	[NO]. Relative.	[NO] <sup>2</sup> . Relative.	Rate of reaction. (mm./100 sec.).	Rate of reaction. Relative.
359	2.38	5.57	150	6.00
300	1.98	4.12	103	3.92
152	1.00	1.00	25	1.00

A corresponding series of experiments made with a fixed initial pressure of hydrogen equal to 300 mm. gave the results

[NO]. (mm.).	[NO]. Relative.	[NO] <sup>2</sup> . Relative.	Rate of reaction. (mm./100 sec.).	Rate of reaction. Relative.
400	1.73	3.00	174	3.86
310	1.34	1.80	92	2.05
232	1.00	1.00	45	1.00

(b) *Hydrogen*. In one series of experiments the initial pressure of nitric oxide was 400 mm.

[H <sub>2</sub> ]. (mm.).	[H <sub>2</sub> ]. Relative.	Rate of reaction (mm./100 sec.).	Rate of reaction. Relative.
289	1.97	160	2.02
205	1.39	110	1.39
147	1.00	79	1.00

In the second series, the pressure of nitric oxide was 300 mm. [The reaction is slower in the ratio  $(300/400)^2$  for equal hydrogen pressures.]

[H <sub>2</sub> ] .....	404	302	244	147	117	104
Rate of reaction .....	103	85	72	59	52	45

These figures give a straight line when plotted, but the line does not pass exactly through the origin. The explanation of this lies in the fact that there is a small amount of surface reaction nearly independent of the pressure of hydrogen. This is what makes the experimentally determined order of reaction slightly less than 3.0. The effect is scarcely noticeable when there is a high pressure of nitric oxide, so that the speed of the gas reaction is great.

*Influence of the Reaction Products.*—We propose to investigate further the influence of inert gases on the rate of reaction. A preliminary investigation of the effect of the reaction products, steam and nitrogen, was made in the following way. Pairs of experiments were selected in which the nitric oxide and hydrogen were present in equimolecular proportions. A curve showing the amount of change at different times was first plotted from the results of the experiment in which the initial pressure was the greater. A point on this curve could be found at which the pressures of unchanged nitric oxide and hydrogen were the same as the initial pressures in the experiment with smaller initial pressures. This point was



used as the origin in plotting the results of the second experiment. The two curves proceeding from the new origin corresponded to reactions taking place under exactly the same conditions except that in one known amounts of the reaction products were present initially. In general, the curves nearly coincided; if anything, the products had a very slight accelerating influence, but it cannot be described as a first-order effect.

*The Termolecular Velocity Coefficients.*—The reaction follows the equation (1). If  $a$  is the initial pressure of nitric oxide and  $b$  that of hydrogen, this becomes

$$dx/dt = k(a-x)^2(b-x),$$

whence

$$kt = \frac{1}{(a-b)^2} \log \frac{b(a-x)}{a(b-x)} + \frac{1}{(a-b)} \left\{ \frac{1}{a} - \frac{1}{a-x} \right\}$$

It is convenient to record results in terms of the period of half-change,  $\tau$ . If hydrogen is in excess, half-change corresponds to  $x = a/2$ . Thus

$$k = \frac{1}{\tau} \left\{ \frac{1}{(b-a)^2} \log \left( \frac{b}{2b-a} \right) + \frac{1}{a(b-a)} \right\}$$

When nitric oxide is in excess, half-change corresponds to  $x = b/2$ . Then

$$k = \frac{1}{\tau} \left\{ \frac{1}{(a-b)^2} \log \left( \frac{2a-b}{a} \right) + \frac{1}{(b-a)} \left( \frac{b}{a(2a-b)} \right) \right\}.$$

Finally, when the two gases are in equimolecular proportions,  $k = 3/(2\tau a^2)$ .

The following table shows the constancy of  $k$  when  $[\text{NO}]$  and  $[\text{H}_2]$  are varied considerably. The temperature was  $826^\circ \text{C}$ .

$[\text{NO}]$ .	$[\text{H}_2]$ .	$\tau$ (secs.).	$k \times 10^7$ .	$[\text{NO}]$ .	$[\text{H}_2]$ .	$\tau$ (secs.).	$k \times 10^7$ .
299	244	112	1.24	110	316	270	1.19
310	302	129	1.19	152	404	204	0.91
300	404	100	1.09	359	400	89	1.12
293	402	100	1.11	144	323.5	227	1.10
406	289	57	1.21	298	280	125	1.35
402	201	46	1.23	181	209.5	264	1.39
405	147	50	1.06	378	376	98	1.08
404	209	49	1.21	370	376	92	1.17
299	147	66	1.60	253	250	180	1.31
175.5	208.5	254	1.50	340.5	340.5	102	1.27
178	220	238	1.45	243	243	176	1.44
232	313	152	1.19	288	288	140	1.29

The increase in  $k$  at lower pressures is due to the existence of the small amount of heterogeneous reaction.

*Influence of Surface.*—The results already described lead us to suspect that a certain amount of surface reaction goes on concurrently with the gaseous change. A series of experiments was

made in a smaller silica bulb containing some powdered silica. A summary of these is given below. The temperature was  $826^{\circ}$  as before.

Av. value of $k$ for expts. in which $[\text{NO}]$ and $[\text{H}_2]$ were both greater than 300 mm. ....	$1.18 \times 10^{-7}$
Compare av. value for larger, empty bulb .....	$1.17 \times 10^{-7}$
Av. value of $k$ for expts. in which $[\text{NO}]$ and $[\text{H}_2]$ were both greater than 200 mm. but not greater than 300 mm. ...	$1.66 \times 10^{-7}$
Compare av. value for corresponding expts. with the empty bulb .....	$1.30 \times 10^{-7}$

This confirms our conclusions, and indicates that at pressures above 300 mm. of each gas the reaction is almost entirely homogeneous.

The smaller bulb was now packed nearly half full with powdered silica. Its catalytic activity towards the decomposition of ammonia—a typical heterogeneous reaction—was about twenty to thirty times greater than that of the larger, empty bulb used in the main series of experiments. At a pressure of 270 mm. of nitric oxide and of hydrogen, the value of  $k$  was now found to be  $2.5 \times 10^{-7}$ , or about doubled, as compared with the twenty- to thirty-fold increase produced in the rate of decomposition of ammonia. The heterogeneous reaction must therefore be a small part of the whole change. These results can only be regarded as qualitative, since the catalysis of the ammonia decomposition is very erratic and cannot be taken as a strictly quantitative measure of the surface area. At temperatures about  $100^{\circ}$  lower, the surface reaction was relatively slightly more in evidence, but not very markedly so.

*Influence of Temperature.*—Three series of experiments were made, two series with the empty bulb, of which the second is the better, since the pressures were higher in all the experiments (greater than 300 mm.), and a third series in the smaller bulb packed with powdered silica. The object of the last series was to find how the proportion of surface reaction varied with temperature, and thus discover what error, if any, would be introduced into the value for the heat of activation determined from the experiments made in the empty bulb.

The first series extended over a range of seven temperatures from  $652^{\circ}$  to  $834^{\circ}$  C. The value of  $E$  was found to be 42,000 calories. The Arrhenius equation was used in the usual manner.

The results of the second series are given below.

$t^{\circ}$ C. ....	$826^{\circ}$	$788^{\circ}$	$751^{\circ}$	$711^{\circ}$	$683^{\circ}$	$631^{\circ}$
$k'$ (av.) .....	476	275	130	59	25.3	5.3

$k'$  is the velocity coefficient expressed, not as before with the concentrations in mm., but with these converted into gram-molecules per litre. The time is in seconds. By plotting  $\log k$  against the reciprocal of  $(t + 273)$  a value of  $E$  is found equal to 44,000

calories. This second value is the better. We adopt it rather than the average value 43,000.

The third series gave the results

$t$ .....	827°	785°	745°	718°	684°
$k'$ .....	1446	692	415	280	90

From these the value found for  $E$  is 39,000 calories. In these last experiments rather more than half the reaction was probably heterogeneous, yet the value of  $E$  was only changed from 44,000 to 39,000 calories. Hence we may conclude that the correction to be applied to the value 44,000 for the small fraction of surface reaction is negligible.

*Conclusion.*—We may therefore conclude that the reaction which takes place at 826° C. between nitric oxide and hydrogen is almost entirely in the gaseous phase, and that the velocity coefficient of the homogeneous reaction is within 10% of  $1.0 \times 10^{-7}$  when the concentrations are expressed in millimetres of mercury and the time in seconds. The heat of activation of the gaseous reaction is 44,000 calories. We consider that it is justifiable to use these values in considerations of the molecular statistics of the reaction. From this point of view the reaction possesses much interest. But the presence of some surface reaction makes it rather unsuitable for studies much more detailed than the general one we have described. We are now investigating the catalytic reaction at the surface of platinum.

### *Summary.*

The interaction of nitric oxide and hydrogen in the region 1000° to 1100° Abs. is a termolecular reaction proceeding in accordance with the equation —  $d[\text{NO}]/dt = k[\text{NO}]^2[\text{H}_2]$ . At pressures above 300 mm. of each of the gases, it is almost entirely homogeneous, but there is a small amount of surface reaction which becomes relatively more important at lower pressures. The heat of activation of the gaseous reaction is 44,000 calories. The molecular statistics of termolecular gaseous reactions are discussed from the point of view of the theory of activation.

It is pointed out that all the termolecular gaseous reactions now known involve the participation of two molecules of nitric oxide.

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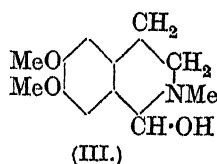
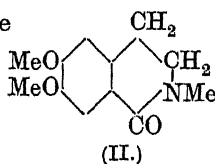
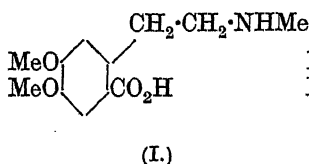
[Received, December 22nd, 1925.]

CIII.—*Synthetical Work on the isoQuinoline Alkaloids.*  
*Part I. Substituted o-Carboxyphenylethylamines.*

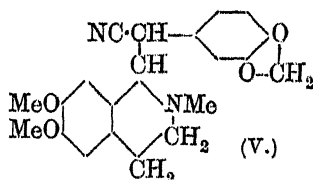
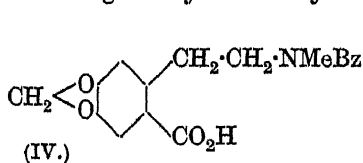
By GEORGE ALFRED EDWARDS.

THIS communication is concerned with the preparation and properties of substances obtained in a preliminary investigation of possible methods of preparing  $\beta$ -(4 : 5-dimethoxy-2-carboxyphenyl)ethyl-methylamine (I), and of similar substances required in connexion with proposed syntheses of alkaloids of the cryptopine type.

Laudanosine appeared to be a possible source of this amino-acid, since Pyman (J., 1909, 95, 1272) had shown that the lactam, 6 : 7-dimethoxy-2-methyldihydroisoquinolone (II), was obtained by its oxidation. He further showed that on more gentle oxidation



1-hydroxy-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline (III) was produced, and that it reacted in many respects like hydrastinine, which differs from it structurally only in containing the methylenedioxy-group in place of the two methoxy-groups. Freund (Ber., 1889, 22, 1156) found that hydrastinine gave a benzoyl derivative in which the tetrahydropyridine ring had presumably been opened, and on oxidation gave what was probably *N*-benzoyl- $\beta$ -(4 : 5-methylenedioxy-2-carboxyphenyl)ethylmethylamine (IV). Attempts to benzoylate substance (III), however, resulted in the conversion of the benzoyl chloride into benzoic anhydride, the  $\psi$ -base acting merely as a catalyst.



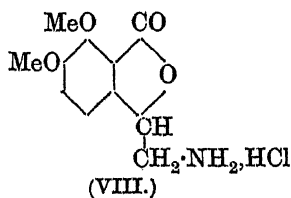
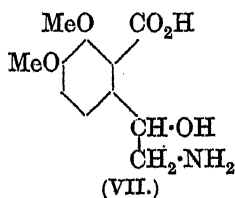
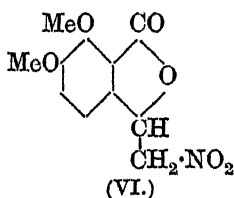
In the proposed synthesis of cryptopine, the substance (I) was to have been esterified and condensed, in presence of sodium ethoxide, with homopiperonylnitrile,  $(\text{CH}_2\text{O}_2)\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CN}$ , or a derivative of it with a substituent in the ortho-position to the  $-\text{CH}_2\cdot\text{CN}$  group. Attempts to prepare this nitrile from homopiperonal by Semmler and Bartelt's method (Ber., 1908, 41, 2751) gave minute yields, valueless for synthetic purposes. Interaction of piperonyl bromide

and alcoholic potassium cyanide led to *piperonyl ethyl ether*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{:O:C}_2\text{H}_5$ . The nitrile was most conveniently prepared by condensing piperonal with hippuric acid, hydrolysing the resulting so-called azlactone to piperonylpyruvic acid (Kropp and Decker, *Ber.*, 1909, **42**, 1188; compare Buck and Perkin, *J.*, 1924, **125**, 1680), and treating the *oxime* of this with acetic anhydride, whereby the nitrile was produced by loss of carbon dioxide and water.

Homopiperonylonitrile condenses with the  $\psi$ -base (III) in warm alcohol. The product, 6:7-dimethoxy-1(3':4'-methylenedioxy- $\omega$ -cyanobenzyl)-2-methyltetrahydroisoquinoline (V) does not give a benzoyl derivative under any of the normal conditions of benzoylation, and after several unsuccessful attempts to open the ring between the 1-carbon atom and the nitrogen, this line of attack was abandoned.

The direct synthesis of the required amino-acid (I) from *m*-opianic acid was next tried. The only suitable method for preparing *m*-opianic acid in the quantities required for synthetic work is that of Fargher and Perkin (*J.*, 1921, **119**, 1724), which makes use of creosole. Only a small quantity of this being available, a preliminary investigation was made with the more readily accessible opianic acid (Edwards, Perkin, and Stoyale, *J.*, 1925, **127**, 197), three methods of converting it into the required type of substance being examined.

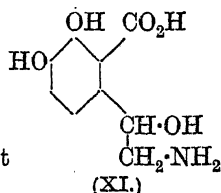
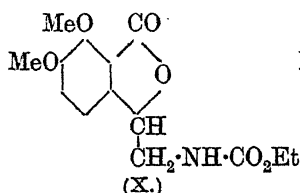
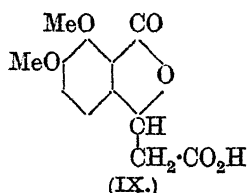
Opianic acid condensed with nitromethane to give a substance (VI) which on reduction yielded the lactone of  $\beta$ -hydroxy- $\beta$ -(2-carboxy-3:4-dimethoxyphenyl)ethylamine hydrochloride (VIII). The base



corresponding to this was formed on treatment with one molecular proportion of cold alkali, whilst hot alkali gave the amino-acid itself (VII). The latter, on being heated alone or in tetralin, lost water and ammonia, leaving a nitrogen-free, resinous substance, and treatment with reagents which attack the amino-group resulted in the formation of derivatives of the amino-lactone (VIII). The poor yields obtained by this method are probably due to the decomposition of the condensation product by the acid reducing agents.

Opianic acid condensed with malonic acid to give meconine-acetic acid (IX) (Liebermann, *Ber.*, 1886, **19**, 2290), the amide of

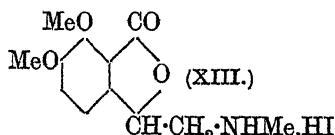
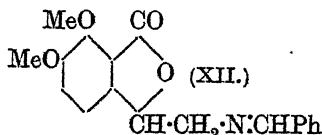
which in the Hofmann reaction, when carried out under the conditions used by Decker (*Annalen*, 1913, **395**, 291) in the preparation of substituted phenylethylamines from phenylpropionamides, gave about a 30% yield of the amino-acid (VII). The alternative Curtius reaction proceeded quite smoothly as far as the carbamate (X), which proved unexpectedly stable towards acid hydrolysing reagents, boiling concentrated hydrochloric acid leaving it unchanged. When the hydrolysis mixture was heated in a sealed tube at 140–150°, hydrolysis of the carbamate was accompanied by that of the two methoxy-groups, the product being  $\beta$ -hydroxy- $\beta$ -(2-carboxy-3:4-dihydroxyphenyl)ethylamine (XI). This is a typical catechol derivative, giving an intense green coloration with ferric chloride and oxidising rapidly in air. It is similar in properties to the amino-acid already described. In the cold, sodium hydroxide



merely opened the lactone ring of the carbamate (X), but a boiling solution removed the carbethoxy-group as well. The resulting solution on careful neutralisation slowly deposited the amino-acid (VII).

Of the three methods discussed above, the Curtius reaction gives the best yield, *viz.*, 40% of the theoretical, calculated on the quantity of opianic acid taken.

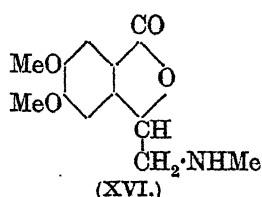
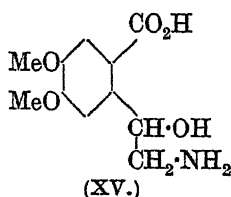
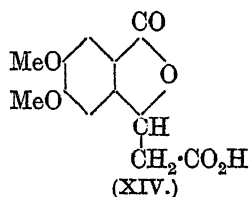
The amino-acid (VII) was converted into the benzylidene compound (XII), the methiodide of which, on hydrolysis, yielded the lactone of  $\beta$ -hydroxy- $\beta$ -(2-carboxy-3:4-dimethoxyphenyl)ethylmethylamine hydriodide (XIII). On opening the lactone ring, the corresponding amino-acid was formed; it at once passed into its lactone on treatment with mineral acids or with reagents which attack the amino-group.



Benzenesulphonyl derivatives of the amino-acids may be prepared by treating the sodium salts with benzenesulphonyl chloride and caustic soda. The dimethylation of the product and the condensation of the ester group with the reactive methylene group in

such substances as phenylacetonitrile and phenylacetic ester will be dealt with in a later paper.

*m*-Opianic acid condensed best with malonic acid when dissolved in pyridine containing a trace of piperidine. The product, *m*-meconineacetic acid (XIV), was converted by the modification of the Curtius reaction already described into  $\beta$ -hydroxy- $\beta$ -(4:5-dimethoxy-2-carboxyphenyl)ethylamine (XV). This was methylated



in the form of its benzylidene derivative, and the final product (derived from its lactone XVI) was precisely similar in properties to the amino-acids already described.

The quantity of creosole available proved sufficient for the production of only about 5 grams of the amino-acid. The production of this substance in quantity from *m*-meconine by another method is being investigated.

# EXPERIMENTAL.

*r*-Laudanosine (*N*-methyltetrahydropapaverine) was obtained in almost quantitative yield by reducing papaverine methosulphate with zinc and alcoholic sulphuric acid. The yield obtained in Pictet and Finkelstein's process (*Ber.*, 1900, 332, 346), *viz.*, reduction of the methiodide with tin and concentrated hydrochloric acid, is about 50%.

The solid obtained by heating papaverine (50 g.) and methyl sulphate (16 c.c.) on the water-bath for 30 minutes was dissolved in boiling water (200 c.c.), mixed with alcoholic sulphuric acid (25 c.c. of 30% solution), and the whole heated on the water-bath while zinc dust and alcoholic sulphuric acid were added alternately so that hydrogen was gently evolved. After 2½ hours, the boiling solution was filtered, the zinc washed thoroughly with boiling alcohol, and the hot solution added slowly to ammonia (350 c.c.; *d* 0.880) mixed with powdered ice. The product separated slowly as a voluminous mass of needles, and after one recrystallisation from dilute alcohol was pure, *m. p.* 115°.

*Piperonyl Ethyl Ether*.—An alcoholic solution of piperonyl bromide (Orr, Robinson, and Williams, *J.*, 1917, 111, 950; Robinson and Robinson, *J.*, 1914, 105, 1463) and excess of sodium ethoxide was warmed on the water-bath for 10 minutes and poured

into water. The *ether*, which was extracted with ether, was a pleasant-smelling oil, b. p. 130—133°/13 mm. (Found: C, 66.4; H, 6.4.  $C_{12}H_{10}O_3$  requires C, 66.7; H, 6.7%).

*Oxime of Piperonylpyruvic Acid*.—A solution of piperonylpyruvic acid and hydroxylamine hydrochloride ( $1\frac{1}{2}$  equivs.) in 8% aqueous sodium hydroxide (3 equivs.) was heated on the water-bath for 1 hour. According as it was acidified with acetic acid or hydrochloric acid the solution deposited the insoluble sodium salt of the oxime or the *oxime* itself. The white, flocculent precipitate of the latter was separated after 12 hours; it crystallised from alcohol in colourless needles, m. p. 174—175° (Found: N, 6.1.  $C_{10}H_9O_5N$  requires N, 6.3%).

*Homopiperonylonitrile*.—The preceding oxime was gently warmed with acetic anhydride (4 parts); the reaction, at first slow, ultimately became very violent, and water-cooling was usually necessary. The product was distilled in a vacuum; the nitrile then passed over as a golden-yellow liquid, b. p. 160°/10 mm. It quickly solidified on treatment with absolute alcohol, and on recrystallisation from dilute alcohol separated in nearly colourless needles, m. p. 49° (Medinger, *Monatsh.*, 1906, 27, 237, gives m. p. 42°) (Found: C, 67.2; H, 4.4; N, 8.5. Calc., C, 67.1; H, 4.3; N, 8.7%).

6 : 7-Dimethoxy-1-(3' : 4'-methylenedioxy- $\omega$ -cyanobenzyl)-2-methyl-tetrahydroisoquinoline (V).—1-Hydroxy-6 : 7-dimethoxy-2-methyl-tetrahydroisoquinoline (III) (Pyman, *loc. cit.*) was dissolved together with homopiperonylonitrile (1 mol.) in hot alcohol. The condensation product separated from the cooled solution in needles, which melted at 171° to a dark red liquid (Found: C, 68.8; H, 6.0.  $C_{21}H_{22}O_4N_2$  requires C, 68.8; H, 6.0%). It is completely decomposed when boiled with caustic soda, and is a moderately strong base. On treatment with formaldehyde, methylal or methylene oxide, high-melting bases are formed. Since these substances were obviously not of the tetrahydroepi~~ber~~berine type, they were not further investigated.

*Synthesis of  $\beta$ -Hydroxy- $\beta$ -(2-carboxy-3 : 4-dimethoxyphenyl)ethyl-methylamine.*

*Reduction of Meconine-nitromethane*.—Meconine-nitromethane (15 g.) was dissolved with cooling in concentrated hydrochloric acid (200 c.c.) containing stannous chloride (42 g.); much heat was generated, and the liquid soon began to deposit a yellow tin salt. After an hour, this was filtered off, washed with hydrochloric acid, dissolved in boiling water, the tin removed with hydrogen sulphide, and the filtrate evaporated to small bulk. The hydrochloride thus obtained crystallised from dilute alcohol in colourless needles, m. p.



248°, and was the lactone of  $\beta$ -hydroxy- $\beta$ -(2-carboxy-3:4-dimethoxyphenyl)ethylamine hydrochloride (VIII) (Found: C, 51.4; H, 5.3.  $C_{11}H_{13}O_4N \cdot HCl$  requires C, 51.0; H, 5.4%).

The *picrate* of the base separated slowly in golden-yellow needles, m. p. 202—204° (decomp.), when a hot solution of the hydrochloride and picric acid in water was cooled.

*Meconineacetamide*.—Meconineacetic acid (Liebermann, *loc. cit.*) (40 g.) was boiled for  $\frac{1}{2}$  hour with thionyl chloride (130 c.c.), the acid chloride crystallising in fine needles. The excess of thionyl chloride was distilled off on a water-bath; the crystalline residue, after being washed with dry ether and dried in a steam-oven, melted at 158—159° and was sufficiently pure for immediate use.

The finely-powdered acid chloride was added slowly to aqueous ammonia (*d* 0.880; 250 c.c.) containing ice. After 1 hour, the white, amorphous product was washed with cold alkali and ether and crystallised from glacial acetic acid; it then separated in colourless masses of prisms, m. p. 223—224°. It was quite insoluble in cold alkalis, but dissolved readily, on warming, with evolution of ammonia. The latter treatment also opened the lactone ring, but all attempts to effect this change without attacking the amino-group were unsuccessful (Found: C, 57.5; H, 5.2; N, 5.6.  $C_{12}H_{13}O_5N$  requires C, 57.3; H, 5.1; N, 5.6%).

The esters of meconineacetic acid may be prepared by cooling a solution of the acid chloride in the minimum amount of the hot alcohol. The methyl ester was thus obtained in colourless hexahedra, m. p. 124°, identical with that obtained by Liebermann (*loc. cit.*) by direct esterification.

*Action of Sodium Hypochlorite upon the Acid Amide*.—The finely-powdered acid amide, suspended in water at 60°, was shaken with exactly 1.2 mols. of sodium hypochlorite. When the solid had dissolved, the liquid was made very strongly alkaline with caustic soda, the temperature allowed to rise slowly to 85°, and, after  $\frac{1}{2}$  hour, the solution was cooled and made just perceptibly acid to litmus by addition of acetic acid.  $\beta$ -Hydroxy- $\beta$ -(2-carboxy-3:4-dimethoxyphenyl)ethylamine (VII) separated slowly as a microcrystalline powder, m. p. 224°. It was insoluble in all non-hydroxylic organic solvents, and very sparingly soluble in boiling alcohol or water. A solution of the crude substance in hot ammonia was filtered from insoluble impurities and boiled; as the ammonia evaporated, the amino-acid slowly separated in colourless needles, m. p. 225°. The substance is more soluble in hot solutions of such inorganic salts as copper sulphate and silver nitrate than in water, but separates from them unchanged (Found: C, 54.5; H, 6.1.  $C_{11}H_{14}O_5$  requires C, 54.8; H, 6.2%).

Treatment of the amino-acid with hydrochloric acid at once converted it into the hydrochloride of the lactone (VIII), identical with the substance obtained from meconine-nitromethane. When the solid hydrochloride was treated with the theoretical quantity of 30% ice-cold caustic soda solution, it was converted into the lactone base, which is a colourless, fishy-smelling oil, very soluble in water but insoluble in non-hydroxylic solvents. The lactone ring was opened by warming with caustic soda solution for a few minutes, and the amino-acid was precipitated on making the solution just perceptibly acid to litmus with acetic acid.

The amino-acid was boiled with acetic anhydride (3 parts) for 10 minutes and the solution was then refluxed for  $\frac{1}{2}$  hour with its own bulk of absolute alcohol, evaporated to one-fourth its volume, and diluted with dry ether. The *acetyl* derivative of the lactone base separated in colourless needles, which crystallised from xylene in star-shaped clusters, m. p.  $155^{\circ}$  (Found: C, 58.6; H, 5.7.  $C_{13}H_{15}O_5N$  requires C, 58.8; H, 5.7%).

*Preparation of the Amino-acid (VII) by means of the Curtius Reaction.*—Meconineacetyl chloride (20 g.) was added slowly to hydrazine hydrate (20 g.) cooled in ice. The resulting thick paste of meconineacetylhydrazide was thoroughly ground and, after 12 hours, dissolved in 8% hydrochloric acid (200 c.c.). A bulky, amorphous precipitate slowly separated. This was filtered off, and the filtrate cooled in ice and treated slowly with sodium nitrite (34 g. in the minimum of water). *Meconineacetyl azide* separated as a white solid (14 g.) and was washed with dry ether and dried in a vacuum desiccator. A small portion recrystallised from dry chloroform separated in colourless needles. It was comparatively stable, losing nitrogen only when heated at its melting point,  $94^{\circ}$ , for a short time (Found: N, 14.7.  $C_{12}H_{11}O_5N_8$  requires N, 15.1%).

When the crude azide was boiled for  $\frac{1}{2}$  hour with absolute alcohol (2 parts), a violent evolution of nitrogen took place; the solution on cooling deposited crystals of the lactone of *ethyl  $\beta$ -hydroxy- $\beta$ -(2-carboxy-3:4-dimethoxyphenyl)ethylcarbamate* (X). It crystallised from methyl alcohol in colourless cubes, m. p.  $131^{\circ}$  (Found: C, 56.9; H, 5.8; N, 4.7.  $C_{14}H_{17}O_6N$  requires C, 56.9; H, 5.8; N, 4.7%).

This carbamate was heated with concentrated hydrochloric acid (6 parts) in a sealed tube at  $150^{\circ}$  for 3 hours. The insoluble liquid thus produced was mainly methyl chloride. The aqueous liquid in the tube was boiled, filtered hot, and allowed to cool,  *$\beta$ -hydroxy- $\beta$ -(2-carboxy-3:4-dihydroxyphenyl)ethylamine hydrochloride* being thus obtained in colourless needles, m. p.  $262-265^{\circ}$ . On treating

this salt with ammonium carbonate, the *amino-acid* (XI) was obtained in colourless needles, m. p. 138–140° (Found: C, 50.3; H, 5.3.  $C_{19}H_{12}O_4N$  requires C, 50.7; H, 4.8%). The amino-acid dissolved readily in warm dilute acids or alkalis, but not in alkali carbonates. It did not form a lactone under the conditions obtaining in the case of the dimethoxy-compound.

The carbamate (12 g.) was dissolved in 15% sodium hydroxide solution (50 c.c.) by heating on the water-bath for  $\frac{1}{2}$  hour. After boiling for 5 minutes, the solution was cooled, filtered, and faintly acidified (litmus) with acetic acid. After 12 hours, the amino-acid (VII) separated as a microcrystalline powder, m. p. 224°. The yield was 7 g. from 20 g. of meconineacetic acid, *i.e.*, 40%.

From the solution obtained by boiling the amino-acid (30 g.) and benzaldehyde (60 c.c.) for 20 minutes the greater part of the excess of benzaldehyde was removed in a vacuum. The residue was mixed with boiling methyl alcohol (220 c.c.); from the filtered cooled solution the *benzylidene* derivative of the lactone base (XII) separated in slightly cream-tinged plates, m. p. 125° (Found: C, 69.2; H, 5.5.  $C_{18}H_{17}O_4N$  requires C, 69.4; H, 5.5%).

The benzylidene compound was heated for 2 hours with its own weight of methyl iodide in a sealed tube at 100°. The orange liquid thus formed set, on cooling, to a mass of yellow needles, which was at once washed with carefully dried benzene and dried in a vacuum desiccator. The *methiodide* thus obtained melted at 180°. It decomposed rapidly in the air with liberation of benzaldehyde. Hydrolysis was best carried out by boiling for a short time with four parts of 95% ethyl alcohol; the filtered solution, on cooling, deposited the *lactone* of  $\beta$ -*hydroxy*- $\beta$ -(2-*carboxy*-3 : 4-*dimethoxyphenyl*) *ethylmethylamine hydriodide* (XIII) in colourless prisms, m. p. 220–222°. The *hydrochloride*, prepared by boiling the hydriodide in chloroform solution with phosphorus pentachloride for 10 minutes, separated from alcohol in felted needles, m. p. 233°. The *nitroso*-compound separated in colourless needles, m. p. 108°, when a warm aqueous solution of the hydrochloride was dropped slowly into an ice-cold solution of excess of sodium nitrite (Found: C, 54.0; H, 5.2; N, 10.7.  $C_{12}H_{14}O_5N_2$  requires C, 54.1; H, 5.2; N, 10.5%). From the solution obtained by shaking the hydrochloride and benzoyl chloride (1 mol.) with aqueous sodium hydroxide (2 mols.) the *benzoyl* derivative separated slowly; the large amount remaining in solution was extracted with ether. The product crystallised from a little methyl alcohol in rhombs, m. p. 106°. This substance is insoluble in cold caustic soda solution, but dissolves readily on warming (Found: C, 67.2; H, 5.7.  $C_{19}H_{19}O_5N$  requires C, 66.9; H, 5.5).

$\beta$ -Hydroxy- $\beta$ -(2-carboxy-3:4-dimethoxyphenyl)ethylmethylamine (VII with NHMe in place of  $\text{NH}_2$ ) was obtained by heating a salt of the amino-lactone on the water-bath with a slight excess of caustic soda solution for  $\frac{1}{2}$  hour and just acidifying the cooled solution with acetic acid. It crystallised slowly from water in colourless plates, m. p. 190—192° (Found: C, 56.2; H, 6.8.  $\text{C}_{12}\text{H}_{17}\text{O}_5\text{N}$  requires C, 56.5; H, 6.6%).

$\beta$ -Hydroxy- $\beta$ -(2-carboxy-4:5-dimethoxyphenyl)ethylmethylamine (XV with NHMe in place of  $\text{NH}_2$ ).

*m*-Meconineacetic Acid.—*m*-Opianic acid (28 g.), malonic acid (35 g.), piperidine (30 drops), and pyridine (100 c.c.) were heated on a water-bath for 6 hours. After boiling for a few minutes, the mixture was cooled and poured into 16% hydrochloric acid (300 c.c.); the product, which separated slowly in clusters of needles, crystallised well from a little glacial acetic acid in colourless needles, m. p. 230—231° (Found: C, 56.8; H, 5.0.  $\text{C}_{12}\text{H}_{12}\text{O}_6$  requires C, 57.1; H, 4.8%).

*m*-Meconineacetyl Chloride.—*m*-Meconineacetic acid was boiled for  $\frac{1}{2}$  hour with twice its weight of thionyl chloride, the excess of solvent was removed in a vacuum, and the yellow, syrupy product was made to crystallise by treatment with dry ether. It separated from dry xylene in colourless prisms, m. p. 103—104°.

*m*-Meconineacetamide was prepared in exactly the same way as meconineacetamide. It separated from much alcohol in clusters of needles, m. p. 240—241° (Found: N, 5.6.  $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}$  requires N, 5.6%).

Ethyl *m*-meconineacetate was produced when the acid chloride was dissolved in a little hot ethyl alcohol, and the product allowed to cool. It separated in fine needles, m. p. 133°. The same substance was obtained by direct esterification (Found: C, 59.8; H, 5.8.  $\text{C}_{14}\text{H}_{16}\text{O}_6$  requires C, 60.0; H, 5.8%). The methyl ester separated from methyl alcohol in colourless plates, m. p. 129°.

*m*-Meconineacetic acid was converted by the method already described into *m*-meconineacetyl azide. This separated as a gummy substance which crystallised from chloroform in clusters of needles, m. p. 100° with evolution of nitrogen (Found: N, 14.8.  $\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}_3$  requires N, 15.1%). Treatment with alcohol converted this into the lactone of ethyl  $\beta$ -hydroxy- $\beta$ -(2-carboxy-4:5-dimethoxyphenyl)ethyl-carbamate, which separated in glistening plates with a pale brown tinge, m. p. 177—178° (Found: C, 56.9; H, 5.8; N, 4.7.  $\text{C}_{14}\text{H}_{17}\text{O}_6\text{N}$  requires C, 56.8; H, 5.6; N, 5.0%). Hydrolysis of this with four times its weight of 12% aqueous caustic soda gave a clear solution which, on being cooled and just acidified with acetic acid, deposited  $\beta$ -hydroxy- $\beta$ -(2-carboxy-4:5-dimethoxyphenyl)ethylamine

(XV) in fine, hexagonal prisms, m. p. 204—205° (Found : C, 54.5; H, 6.0.  $C_{11}H_{14}O_5N$  requires C, 54.8; H, 6.2%). The acid readily formed a *benzylidene* compound in the manner described above, which crystallised from methyl alcohol in colourless needles, m. p. 146° (Found : C, 69.1; H, 5.7.  $C_{18}H_{17}O_4$  requires C, 69.4; H, 5.5%). When quite dry, the latter added on methyl iodide in the manner already described, and the *methiodide* was hydrolysed on treatment with hot dilute alcohol to the lactone of  $\beta$ -hydroxy- $\beta$ -(2-carboxy-4 : 5-dimethoxyphenyl)ethylmethylamine (XVI), which crystallised from ethyl alcohol in colourless prisms, m. p. 230—231°. Treatment of this with caustic soda solution opened the lactone ring and produced the amino-acid, which was purified by boiling its solution in ammonia until no more crystals separated. It was thus obtained in needles, m. p. 199—204° (decomp.) (Found : C, 56.9; H, 6.8.  $C_{12}H_{17}O_5N$  requires C, 56.5; H, 6.6%).

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#### CIV.—The Electrometric Titration of Halides.

By WALTER CLARK.

THE object of the experiments to be described was to examine the possibility of applying electrometric methods to the analysis of mixtures of soluble halides and of mixed silver halides, in particular where one halide is present in small proportion—less than 1%—in the other.

The estimation of a single soluble halide by titration with silver nitrate, or conversely of silver ions by titration with a halide solution, can be accurately and simply carried out electrometrically (compare Behrend, *Z. physikal. Chem.*, 1893, **11**, 466; Dutoit and von Weise, *J. Chim. Phys.*, 1911, **9**, 578, 608, 630). For this purpose several different methods have been devised. Certain of these have been summarised by Kolthoff (*Chem. Weekblad*, 1920, **17**, 659), Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2504), and Müller ("Elektrometrische Massanalyse," 2nd edn, 1923).

The most exact method of titration is that in which the titration beaker containing the halide solution and a silver electrode is

connected with a normal electrode, and the *E.M.F.* of the combination is measured after each addition of silver nitrate, the end-point of the titration being taken as the point of maximum rate of change of *E.M.F.* with silver ion added.

In an arrangement due to Pinkhof (*Diss.*, Amsterdam, 1919; *Chem. Weekblad*, 1919, 16, 1163; *Pharm. Weekblad*, 1919, 56, 1218) the normal electrode is replaced by a compensation electrode whose potential is equal to that of the titration system at the end-point. With this method a different compensation electrode would be required for each halide titrated, and in the titration of mixed halides the electrode would have to be changed during the course of the titration.

A variation of Pinkhof's method has been used extensively by Treadwell (*Helv. Chim. Acta*, 1919, 2, 672, 680), and a modification for use with 5 c.c. of solution to be titrated, has been described by Garner and Waters (*J. Soc. Chem. Ind.*, 1922, 41, 337t).

A further method of titration consists in the use of "bimetallic electrode systems," introduced by Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, 44, 2504, 2516; 1923, 45, 623), and suggested also by Müller (*Z. Elektrochem.*, 1924, 30, 420) and Hostetter and Roberts (*J. Amer. Chem. Soc.*, 1919, 41, 1343). This method has been applied also to acid-alkali titrations by van der Meulen and Wilcoxon (*Ind. Eng. Chem.*, 1923, 15, 62) and by Brännich (*ibid.*, 1925, 17, 631).

Another method of titrating soluble halides has recently been described and is worthy of note. In the "differential titration" method of Cox (*J. Amer. Chem. Soc.*, 1925, 47, 2138) the halide solution is divided equally between two beakers joined by an ammonium nitrate bridge and each containing a silver electrode connected with the potentiometer. Both solutions are titrated simultaneously with silver nitrate, one being kept slightly in advance of the other, and the potential is read after each addition of silver. The titration curve obtained is the first derivative of the normal titration curve, and its maximum is the end-point.

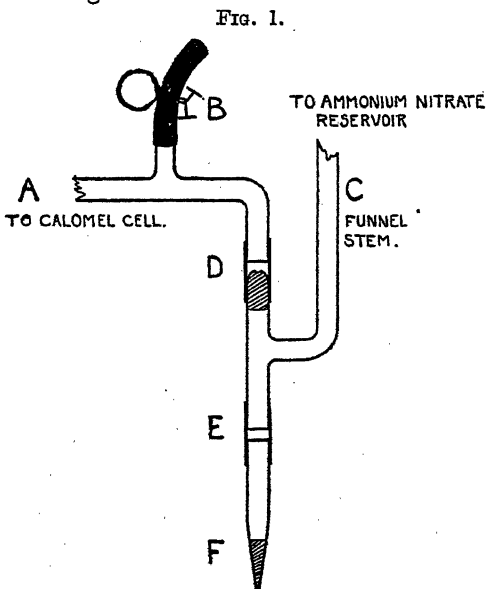
In the investigation to be described the first method of titration was used, *i.e.*, that in which the solution to be titrated contained a silver electrode and was united with a calomel cell, the *E.M.F.* of the combination being measured by means of a potentiometer after each addition of silver nitrate. This method was used because it is quite straightforward and can be used for the titration of mixed halides without changing the electrode or the constant half-cell. It was examined first with a view to its utility for the accurate yet simple estimation of mixtures of two or three alkali halides by direct titration with silver nitrate solution, and then for estimating

mixtures of silver halides. In a few instances, other methods of titration were tested.

### EXPERIMENTAL.

The calomel cell employed was of the saturated potassium chloride type. This was united with the halogen solution to be titrated by a saturated ammonium nitrate bridge in such a way as to prevent diffusion of chloride from the cell into the titration beaker, and to prevent loss of halide from the solution to be titrated by displacement with the specifically heavier ammonium nitrate solution. The arrangement is shown in Fig. 1.

A is a continuation of the side arm of the calomel cell. In the cell itself a wad of glass wool is placed over the surface of the calomel to prevent its disturbance when flushing out with fresh potassium chloride solution. At B is a side tube with clip to allow of the easy removal of air or old potassium chloride from the tube A D when filling it or when renewing the potassium chloride solution. An ordinary separating funnel is used as a reservoir for the saturated ammonium nitrate.



The end of its stem, C, is bent at right angles and a T-piece, D E, is joined on so that D E is parallel to the stem of the funnel. At the upper end, D, the T-piece is constricted, leaving an orifice about 1 mm. in diameter. This partially closed end D is packed tightly to a depth of 1 cm. with filter-paper, previously moistened with ammonium nitrate solution. The lower end, E, of the T-piece is joined by rubber tubing to a drawn-out tube, F, which is immersed in the solution to be titrated. The tapered end of F is also packed tightly to a depth of 1 cm. with a wad of filter-paper moistened with ammonium nitrate solution. The calomel cell is connected with the ammonium nitrate bridge at D by a short piece of rubber tubing.

By means of the side tube and clip at B it is possible to flush out the calomel cell with fresh potassium chloride solution without disturbing the ammonium nitrate bridge. By removing the tube F the nitrate bridge can be flushed out from the reservoir above without disturbing the calomel cell. It is not necessary to change the wad of filter-paper at D often, but the tube F should be changed frequently.

Observations showed that in the course of several hours no chloride reached the titration solution from the calomel cell, and no loss of chloride from the titration solution into the bridge could be detected.

The solution to be titrated was stirred by a motor-driven stirrer at 200 revolutions per minute.

For the silver electrode, No. 20 gauge fine silver wire, provided by Messrs. Johnson Matthey, was used. For the best results it has to be specially treated, as described later. A Cambridge and Paul potentiometer, giving readings to 0.5 millivolt, was used for measuring electromotive forces.

The method of titration was to run standard silver nitrate solution *drop by drop* into the stirred solution of halide, the *E.M.F.* being read after each addition of 1 c.c. When the *E.M.F.* began to rise more rapidly, only 0.1 c.c. of silver nitrate solution was added. When great accuracy was desired, or when only small amounts of halide were being titrated, silver nitrate was added from a micro-burette, or more generally, a *N*/100- or *N*/1000-solution was used, in the neighbourhood of the end-point.

In most cases, a certain time was necessary for establishment of equilibrium of *E.M.F.* in the immediate neighbourhood of the end-point. This will be considered in the course of the description of the titration. The end-point of the titration was obtained either by plotting the titration curve of c.c. of silver nitrate added against *E.M.F.*, and determining its point of inflexion or the mid-point of the maximum slope, or, more readily, by plotting the first derivative of the titration curve, *i.e.*,  $dE/dV$ , against *V*, where *E* is the *E.M.F.* corresponding to a volume *V* of silver nitrate added (compare, for example, Hostetter and Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1341). Each of these methods of determining the end-point was used as occasion demanded, for in certain forms of titration curve one method is preferable to another.

#### *Titration of Solutions of Soluble Halides.*

*Preparation of Pure Materials.*—Silver nitrate solutions of *N*/10, *N*/100 and *N*/1000 strength were made up from Johnson's "pure



triple crystallised silver nitrate," which is specially prepared for the manufacture of photographic emulsions.

Potassium chloride, free from other halides, was available as a commercial product, and approximately *N*/10-solutions were prepared.

No commercial sample of bromide or iodide free from chloride was available. Many samples of ammonium and potassium bromide, and of ammonium, barium, cadmium, and potassium iodide were examined quantitatively for chlorides. The proportion present varied with different samples from 0.2% to about 5%, and with a number of samples of any one salt from any one manufacturer, wide variations were found. Potassium bromide was the worst offender in this respect.

*Preparation of Pure Bromide.*—A sample of potassium bromide, free from chloride and bromate, was prepared by heating once-recrystallised potassium bromate in a silica basin, extracting the fused salt with water, and evaporating the solution to dryness.

Ammonium bromide free from chloride was prepared from purified ammonia and bromine. A sample of commercial ammonia solution, labelled "sp. gr. 0.880, extra pure," contained a trace of chloride which was removed by boiling off the ammonia gas and reabsorbing it in distilled water.\*

For the preparation of pure bromine, the purest commercial bromine, which contained some chlorine, was used. 100 G. were shaken with 50 c.c. of concentrated potassium bromide solution, and then distilled off on a water-bath at 70–90°. The distilling apparatus was made entirely of glass, and the receiver was cooled in ice.

The yield of 70 g. of bromine was well shaken with 5 c.c. of *N*-caustic soda solution and distilled again in the same apparatus (compare Scott, J., 1913, 103, 847; Baxter, *Proc. Amer. Acad. Arts Sci.*, 1906, 42, 201).

Ammonium bromide was made by adding the bromine drop by drop, shaking after each addition, to freshly-distilled ammonia contained in an ice-cooled flask until there was only a slight excess of ammonia. This excess was boiled off and the solution evaporated to dryness. The product was free from chloride and bromate.

*Preparation of Pure Iodide.*—Baxter (*Proc. Amer. Acad. Arts Sci.*, 1903, 39, 249; 1904, 40, 419; 1906, 42, 201) has described the conditions for the preparation of pure bromine and iodine. The method he adopted in the case of iodine did not give successful results in the author's hands. Also attempts were made to prepare

\* Addition of a few drops of silver nitrate solution to the ammonia before distillation ensures the freedom of the final product from chloride.

pure ammonium iodide somewhat on the lines described by Baxter, but without success. It was found impossible to remove the last traces of chloride; under the conditions employed, between 0.1% and 0.2% chloride remained.

Some of the earlier experiments on electrometric titrations, to be described later, suggested a method for the preparation of iodide free from chloride which was very satisfactory and simple. It is briefly as follows :

Ordinary commercial potassium iodide is dissolved in a 5% solution of chloride-free barium nitrate (sodium nitrate, ammonium nitrate or sodium acetate may also be used) and silver nitrate solution is run in slowly drop by drop, with vigorous stirring, a marked excess of soluble halide, however, being left finally. This excess must be larger than the equivalent of chloride present. Silver equivalent to 90% of the iodide was used in the actual preparations. Under these conditions, the precipitate consists entirely of silver iodide and all the chloride remains in solution. The silver iodide precipitate is removed and washed several times with water. It is then suspended in water, stirred vigorously, and reduced with hydroxylamine sulphate\* and chloride-free caustic soda prepared from metallic sodium by the action of water vapour. This gives a precipitate of spongy silver, and a solution of sodium iodide, hydroxylamine, sodium hydroxide, and sodium sulphate. The liquid is filtered, evaporated to dryness, the residue is heated at about 200° to destroy the excess of hydroxylamine,† and extracted with water, and the solution neutralised with sulphuric acid. The solution of sodium iodide and sodium sulphate obtained in this way was suitable for the purpose of electrometric titration; in fact, the presence of sodium sulphate was found to be beneficial to the titration. The solutions obtained were absolutely free from chloride.

If it is desired to have pure iodide, free from sodium sulphate, the solution can be treated with permanganate, and the iodine distilled off and converted into hydriodic acid with hydrogen sulphide gas according to the method of Baxter (*loc. cit.*).

If the product still contains chloride, the iodide-sulphate solution can be again partly precipitated as silver iodide, followed by reduction as described, but in no case has more than one precipitation and reduction been found necessary.

Stock solutions of bromide and iodide of practically *N*/10-strength were prepared, and standardised against the stock *N*/10-silver nitrate solution, by the dye-indicator method of Fajans

\* This can be obtained commercially quite free from chloride.

† Alternatively, an excess of silver iodide is used so that there is no excess of hydroxylamine.

and Hassel (*Z. Elektrochem.*, 1923, 29, 495; *Kolloid Z.*, 1924, 34, 304), fluorescein being used as indicator. The stock chloride solution was standardised by the normal titration method, with chromate as indicator.

In the titration of silver ions with halide ions, with fluorescein as indicator, it is essential to define the conditions rather closely, otherwise the true end-point is difficult to determine. It is necessary to titrate in very dilute solution, with a low concentration of dye. For example, in the titration of *N*/10-silver nitrate with *N*/10-potassium bromide it was found best to dilute 10 c.c. of the silver nitrate to about 200 c.c. with water, and use 5 drops of a 1 : 2000 solution of fluorescein as indicator. In these conditions, the silver halide does not coagulate in the neighbourhood of the end-point, and the change from rose colour to yellowish-green is sharp and readily located.

#### *Electrometric Titration of Halides.*

The solutions of soluble halides were titrated electrometrically with a standard silver nitrate solution, and the results agreed identically with those obtained by the ordinary titrations. For any further stock solutions prepared, standardisation was therefore carried out by the electrometric method.

In the titration of the single halide solutions with silver nitrate, the magnitude of the potential jumps about the end-point was roughly : for chloride, 180 mv. ; for bromide, 350 mv. ; for iodide, 500 mv., being bigger the lower the solubility of the corresponding silver salt.

The procedure in titration was to dilute the volume of halide taken to 50 c.c. in some cases, or to 150 c.c. in other cases, with water or any required solution, and then to titrate with the *N*/10-silver nitrate.

In the titration of bromide or iodide, no anomalies were observed which could be ascribed to the nature of the silver electrode employed. In the case of chlorides, however, certain peculiarities were observed which were shown to be dependent on the electrode surface.

#### *Effects Due to the Electrode.*

The first electrodes used were cleaned by scraping with emery cloth or a knife blade. In the titration of chlorides, the addition of the first drop of silver nitrate resulted in a sudden rise in potential. This jump was by no means constant, being about 40–50 mv. in certain cases, and less than 10 mv. in others. With a higher concentration of chloride, a bigger jump was sometimes observed, and its magnitude was dependent to some extent on the presence of

neutral salts. Carrying out the titration in red light did not improve matters. The jump was not due to the presence of a trace of bromide or iodide in the chloride, since its magnitude was variable for the same amount of chloride used, but was due to some peculiarity of the silver electrode, since it varied with the nature of the silver surface.

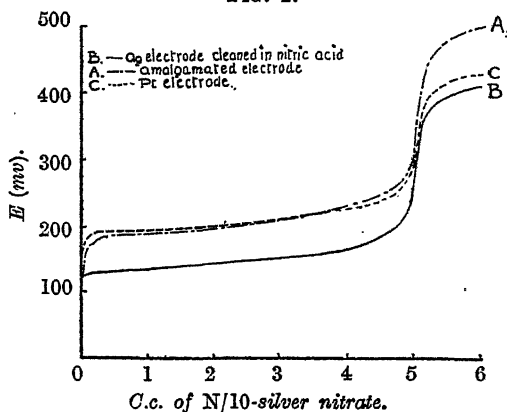
To avoid any confusion in the event of the possibility of the presence of a trace of iodide or bromide in the chloride, the conditions for obtaining an electrode which did not give the initial jump were studied. A long series of experiments showed that plating the electrode from a potassium argentocyanide solution does not give a reproducible electrode which comes into equilibrium with the chloride immediately. Various other methods of treatment showed that if the electrode was first cleaned with emery cloth and then immersed, until gassing freely, in a solution of nitric acid (1 : 1) to which a little sodium nitrite had been added, it assumed equilibrium immediately on being immersed in the chloride solution, and the potential alteration on addition of the first drop of silver nitrate was very small—never more than about 8 millivolts. Electrodes treated in this way are quite trustworthy, and were used for all the electrometric titrations.

The effect of amalgamating the electrode was next tried. Amalgamation was effected by cleaning the electrode with emery cloth and then rubbing it with mercury by means of a wad of cotton wool on a glass rod, under dilute nitric acid. With such an electrode equilibrium was established in a very short time, but the first addition of silver nitrate produced a big jump in potential, equal to 70 mv. After this, the titration curve proceeded in a normal manner, giving the same end-point as the plain silver electrode. The whole curve, however, was shifted in the direction of a higher *E.M.F.* compared with the plain silver electrode curve; *i.e.*, it was more "noble." This is shown in Fig. 2. Similar results were obtained in the titration of bromides and iodides.

This suggested a new method of titrating halides with silver nitrate by means of a bimetallic electrode system, the use of a calomel cell thus being eliminated. If two electrodes, one of amalgamated silver and the other of plain silver, are immersed in a chloride solution to be titrated, the resulting titration curve should be the difference between curves A and B in Fig. 2. This difference is practically constant until, in the neighbourhood of the end-point, a deviation occurs, giving a sharp break in the curve, after which it becomes constant again. Measurements showed that this method affords a means of determining a halide as accurately as the other methods used. The breaks at the end-point are very sharp and the magnitude

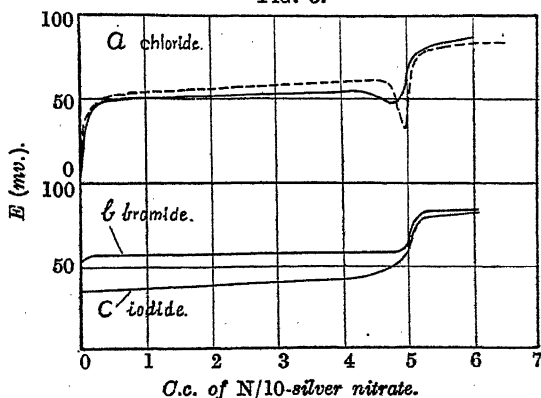
of the jumps in the case of chloride, bromide, and iodide are about 30–40 mv. Fig. 3 shows titration curves for chloride, bromide, and iodide. In the neighbourhood of the end-point, it is necessary to allow a minute or so for equilibrium to be attained after each addition of silver ions.

FIG. 2.



The dotted curve in Fig. 3 (a) is the curve calculated by subtracting the two curves A and B of Fig. 2. It agrees well with the curve obtained by direct titration with the bimetallic system. In the case of chloride only, a drop in the curve is observed in many cases,

FIG. 3.



before the final jump, although in some chloride titrations this drop is absent. The end-point of curves which exhibit this drop is at the point of maximum slope of the final jump. All curves obtained by this bimetallic method exhibit an initial jump on the first addition of silver ions, owing to the amalgamated electrode always

showing such a rise. The method has not yet been applied to mixtures of halides. In the titration of iodides, the curves with plain silver and with amalgamated silver were actually coincident for some distance at the end-point, and yet the bimetallic titration showed a marked jump at the end-point. Müller (*Z. Elektrochem.*, 1924, 30, 420) appears to think that if the curves are tangential the potential should drop to zero at the end-point; but this is not necessarily so.

In many cases of normal titration with a silver wire and calomel cell, some time, often  $\frac{1}{2}$  hour, is required for the attainment of equilibrium of *E.M.F.* in the immediate neighbourhood of an end-point, especially in titrations with very dilute silver nitrate. During this time, the potential rises, rapidly at first, then more slowly, and finally reaches a steady value. This change corresponds with what is equivalent to a slow increase in silver-ion concentration, and obviously is not due, therefore, to the silver ions taking a long time to react with the halide ions remaining. It appears to be due to the time taken for the silver electrode to assume equilibrium with the changed concentration of silver ion.

If an electrode which has been used for one titration of halide is not scraped clean and treated with nitric acid before being used again, the *E.M.F.* found for the new system before the addition of any silver ions is somewhat higher than when a freshly-cleaned electrode is used, and the initial potential jump is very small. The electrode seems to be "formed" in some way, during the first titration.

Good titration curves giving correct end-points are obtained if a bright platinum wire instead of a silver wire is used in conjunction with a calomel cell (compare Müller, *Z. Elektrochem.*, 1924, 30, 420). The curve shows an initial jump of about 40 mv., and lies above the curve for the silver electrode, as shown in Fig. 2. Attempts to use a bimetallic electrode system of platinum and silver gave very poor results, which were useless in practice.

#### *Titration of Mixed Halides.*

The solubility products of the silver halides are of the order : silver chloride,  $10^{-10}$ ; silver bromide,  $10^{-12}$ ; silver iodide,  $10^{-16}$ . Theoretically, then, if silver nitrate is added slowly to a mixture of, say, bromide and chloride in solution, precipitation of the bromide should be complete before that of the chloride begins. In practice, this does not occur; some chloride is precipitated along with the bromide before all the bromide is thrown down, and if a mixture of bromide and chloride in water is titrated electrometrically with silver nitrate, an error in the values is found.

That the individual halides cannot be separated quantitatively from a mixture of halides by addition of silver nitrate has long been known. It has been commented on by many workers, including Foerster ("Elektrochemie Wässrige Lösungen," 3rd edn, 1922, p. 165), Mellor ("Treatise on Inorganic Chemistry," Vol. III, pp. 418—419), Sheppard and Trivelli ("Silver Bromide Grain of Photographic Emulsions," 1921, pp. 42 *et seq.*), Küster (*Z. anorg. Chem.*, 1898, **19**, 81), Küster and Thiel (*ibid.*, 1900, **23**, 25), Thiel (*ibid.*, 1900, **24**, 1), and Müller ("Elektrometrische Massanalyse," 2nd edn, 1923).

The electrometric titration curve of a mixture of two or three soluble halides with silver nitrate shows a sudden break in the neighbourhood of the end-point of each halide, the iodide break occurring before the bromide break, which comes before the final chloride break. The arguments which apply to any pair of halides are obviously applicable to titration of a mixture of all three, so only pairs of halides will be considered at first. If a mixture of chloride and bromide in water, with no other additions, is titrated with silver nitrate, the bromide end-point appears too late, whilst the final break appears in its true position. This results in a correct estimate of the total halide, but a too high value for bromide and a too low value for chloride. The same applies in the case of bromide-iodide mixtures. With chloride-iodide mixtures the error is practically non-existent. It seems to be the general opinion that the end-point error is due to the formation of solid solutions as described by Küster and Thiel (*loc. cit.*), adsorption phenomena playing a preliminary rôle.

According to Dutoit and von Weisse (*J. Chim. Phys.*, 1911, **9**, 630) iodide can be accurately titrated in presence of a large excess (600 times or more) of chloride or bromide. This is true for iodide in chloride, but certainly not for iodide in bromide.

The end-point error increases in the series: chloride-iodide < bromide-iodide < chloride-bromide, being larger the less the solubility difference between the silver salts corresponding with a pair of halides. The magnitude of the error in the case of bromide-chloride and bromide-iodide mixtures is indicated by the following figures :

C.c. of halide solutions in terms of *N*/10-silver nitrate.

Theoretical.		Found.	
Chloride.	Bromide.	Chloride.	Bromide.
{ 5.05	5.05	4.5	5.6
{ 5.05	5.05	4.6	5.5
Bromide.	Iodide.	Bromide.	Iodide.
{ 5.15	5.05	5.0	5.2
{ 5.15	5.05	5.0	5.2

Two methods were tried for eliminating this error, namely : ( 1 ) working in very dilute solution, and ( 2 ) adding certain neutral substances to the titration solution.

The effect of dilution was examined on the titration of a bromide-iodide mixture. Diluting to 330 c.c. instead of the 50 c.c. normally employed in the titrations resulted in an increase in the error.

The correction of the end-point error by adding ions which are strongly adsorbed by silver halides has been studied in detail by Müller (*op. cit.*), who titrated in the presence of 5% barium nitrate solution and found that this salt prevents, or at any rate limits, the formation of solid solutions, so that the end-point error is practically eliminated. Müller writes : "The accuracy of estimation of iodide in the presence of bromide and of iodide in the presence of chloride is good in all cases in presence of 5% barium nitrate. Even the estimation of small amounts of one halide in presence of excess of the other is not affected. . . . In the estimation of bromide and chloride in the presence of one another, we must, unfortunately, reckon on an error of 1% too much bromide and correspondingly too little chloride, if equal molar concentrations of both are taken. This error increases with increasing excess of chloride, and falls off with increasing bromide excess . . . until it can be neglected when the molar concentration of bromide exceeds that of chloride by five times." Müller also mentions potassium alum in the same connexion as barium nitrate, but gives no data concerning its action. According to Foerster (*op. cit.*), in presence of barium nitrate, iodide in a ratio of iodide : bromide  $> 1 : 3600$  can be estimated accurately, but bromide in chloride only when bromide : chloride = 1 : 10.

It appears that adsorption effects of some type are responsible for the end-point error. The exact nature of this adsorption is not quite clear, although it is probable that in the case of iodide-bromide mixtures, for example, it is adsorption of silver bromide to silver iodide which is concerned. It cannot be mere adsorption of bromide ions, because a certain amount of silver ions is involved ; also it is improbable that it is adsorption of silver ions alone. It is most likely adsorption of silver bromide itself (probably colloidal), rather than the formation of a solid solution in the usually accepted sense.

Numerous measurements substantiated Müller's observations that correct end-points are obtained in presence of 5% barium nitrate solution. Lottermoser used ammonium nitrate to remove adsorbed silver from silver halides, and Fajans and his co-workers (Fajans and Hassel, *Z. Elektrochem.*, 1923, 29, 495; Hassel, *Kolloid-Z.*, 1924, 34, 304) studied the adsorption of dyes, and

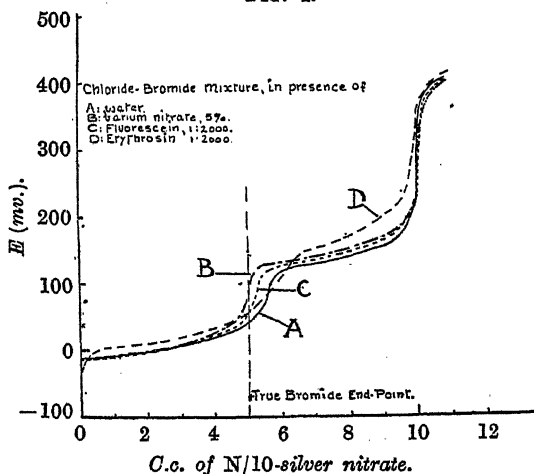






adsorption replacement by dyes, on silver halides, with particular reference to a titration method for halogen and silver using fluorescein and its halogen-substitution products as indicators. These and other substances, including some which are known to be strongly adsorbed by silver halides, were investigated by the author. Since the end-point error is most marked in the case of bromide-chloride mixtures, in some cases only this mixture was investigated; in others, iodide-bromide mixtures were studied as well. The method of examination in most instances was to titrate with  $N/10$ -silver nitrate a mixture of 5.0 c.c. of a  $N/10$ -solution of each of the halides in the presence of 50 c.c. of the solution of the substance investigated.

FIG. 4.



**Dyestuffs.**—Erythrosin (1 in 2000), fluorescein (1 in 2000), and rose Bengal 3 (1 in 2000) gave correct end-points with the bromide-iodide mixtures. In the case of the chloride-bromide mixture, fluorescein (1 in 2000) gave a partial correction, as shown in curve C, Fig. 4. With erythrosin (1 in 2000), the final end-point for the mixture was accurate and was marked by a definite jump in potential, but the first break, representing the bromide end-point, was flattened out. In Fig. 4, curve D is a titration curve obtained in presence of erythrosin (1 in 2000). Similar results were obtained in presence of safranin (Bayer, 1 in 1000). Curve A (Fig. 4) shows the curve in presence of water alone, and curve B the correct curve, in presence of 5% barium nitrate.

Correct end-points for both chloride-bromide and bromide-iodide mixtures were obtained with 5% solutions, not only of

CO\*

barium nitrate, but also of ammonium nitrate, sodium nitrate, and sodium acetate. The results with sodium acetate show that the effect is not due to the nitrate ion, and this was confirmed when it was found that *N*-sulphuric acid also gave practically complete correction.

A solution of 3.5*N*-nitric acid, with a platinum electrode, gives correct end-points with bromide-chloride mixtures, but at the final break the curve begins to rise sharply and then drops suddenly back, after which it tends to become horizontal. The system is rather insensitive and the potential readings are jerky and can be read only to the nearest 2 or 3 millivolts.

*N*/10-Nitric acid, with a silver electrode, gives correct end-points, and is very sensitive. For accurate work, involving a long titration time, it is conceivable that an error could be introduced owing to action of the acid on the silver electrode, but with ordinary titrations of a mixture of equivalent proportions, no error was observed. A platinum electrode is unsatisfactory with *N*/10-nitric acid.

It follows from the foregoing that although the presence of certain dyes is beneficial in the case of bromide-iodide mixtures, they are not of general value. On the other hand, barium, sodium, and ammonium nitrate, and sodium acetate in 5% solution give correct end-points with bromide-chloride and bromide-iodide mixtures for a wide variation in the proportions of the constituents of the mixtures. The presence of these salts curtails the titration time by increasing the sensitiveness of titration and lowering the time required for equilibrium potential in the region of the end-points; even for the titration of a single halide in solution their presence is beneficial. In absence of added salts, the silver halides formed in the titration remain in colloidal suspension until the final end-point is reached; if a salt is present, however, the silver halides begin to precipitate shortly after the first addition of silver nitrate.

The original object of this investigation was to study the applicability of electrometric methods to the examination of materials used in the manufacture of photographic emulsions, and to the analysis of emulsions themselves. In all the titrations made, this object was borne in mind. Consequently, in the examination of bromide-iodide mixtures, for example, low percentages of iodide in bromide were considered, rather than low percentages of bromide. A series of mixtures was studied in various circumstances to ascertain if it was easy to estimate a low percentage of one halide in the other. A limit of 0.2% of iodide in bromide and of chloride in bromide was set. The following table shows some results of measurements. The percentage composition refers to equivalents of one halide in another. The substances mentioned in the column

headed "Notes" were added to the electrolyte, 50 c.c. of a 5% solution being used in each case.

Mixture taken.	Vol. in c.c. of <i>N</i> /10-conc.	Found.	Notes.
100% Bromide.	5, 10	100% Bromide.	Same results in water, barium nitrate, sodium acetate, etc. Barium nitrate, etc., <i>must</i> be present.
100% Chloride.	5, 10	100% Chloride.	
100% Iodide.	5, 10	100% Iodide.	
50% Chloride in bromide.	10	50% Chloride.	
1.01% Chloride in bromide.	10	0.99% "	Barium nitrate.
0.51% " "	10	" ?	Sodium acetate; breaks in curve not separated.
0.50% " "	20	0.50% "	Barium nitrate.
0.2% " "	50	<0.25% "	Sodium acetate.
		about	
0.2% " "	50	0.1% "	" "
0.2% " "	100	0.19% "	" "
0.2% " "	100	0.22% "	Barium nitrate.
50% Iodide in bromide.	10	50% Iodide.	Barium nitrate, etc.
1.6% " "	10	1.5% "	Barium nitrate.
0.19% " "	10	0.2% "	" "
50% Chloride in iodide.	10	50% Chloride.	In water alone; more sensitive in presence of barium nitrate, etc.
0.2% " "	50	0.2% "	75 C.c. of 5% am- monium nitrate.
0.2% " "	50	0.18% "	75 C.c. of 5% am- monium nitrate.

The table shows that it is possible to estimate 0.2% chloride in bromide or iodide, and 0.2% iodide in bromide, with a fair degree of accuracy. The bulk of the halide was precipitated with *N*/10-silver nitrate, but for the estimation of halide present in the proportion of 1% or less, *N*/100- or *N*/1000-silver nitrate was used, an *N*/10-solution being employed only for precipitating the bulk of the halide in excess. The accuracy of estimation of a small percentage of one halide obviously depends on its absolute amount. If the absolute amount is too small, it becomes impossible to estimate the chloride present in low ratio at all, because no distinction is observed between the two breaks in the curve. Using a mixture of *N*/10-strength, it is possible to estimate 0.2% chloride in iodide with 50 c.c., but in the case of 0.2% chloride in bromide, if 50 c.c. are used the breaks in the curve are not separated, and at least 100 c.c. must be taken.

The estimation of low percentages of chloride in iodide or bromide thus involves taking a big bulk of material; this makes the titration very long, and introduces a possible source of error in that some of the chloride solution may be occluded in the bulky silver bromide or silver iodide precipitate. Means were therefore sought by which

the bromide or iodide could be destroyed, at the same time leaving the chloride free in the solution, where it could be titrated.

Numerous methods have been devised for estimating mixtures of halides in which one halogen is removed by oxidation of its halide salt, leaving the other halide intact. Considering a chloride-bromide mixture, however, it is very probable that in the region of the point where practically all the bromide had been destroyed, some of the chloride would be attacked as well. A satisfactory method of operation would be to react with insufficient oxidiser to destroy all the bromide present, leaving, say, equal proportions of bromide and chloride, and then to titrate this mixture electrometrically in the usual way. In this manner, a big bulk of mixture, in which the absolute amount of chloride is high enough for the accuracy required, can be used without the disadvantages already mentioned. There seems theoretically to be no limit to the minuteness of the trace of chloride which could be estimated in this way.

Attempts to destroy all the bromide by means of ammonium persulphate (Engel. Compare Crookes's "Select Methods in Chemical Analysis," 1905, p. 558) or potassium permanganate (Winkler, *Z. angew. Chem.*, 1915, 28, 477, 494) were not successful. In the former case all the bromide could not be destroyed, even when many times the theoretical quantity of persulphate was used, whilst in the latter case some chlorine was always lost in getting rid of the last traces of bromide. For example, a mixture of 2.3800 g. of pure potassium bromide with 0.0050 g. of potassium chloride in 350 c.c. of water was analysed by Winkler's permanganate method, and 0.0038 g. of chloride was found instead of 0.0050 g.

Using just insufficient permanganate to react with all the bromide proved to be a very suitable and accurate means of determining low percentages of chloride in iodide and bromide. The procedure is best illustrated by an actual example, as follows: A mixture of 2.3800 g. of potassium bromide and 0.0050 g. of potassium chloride was dissolved in 350 c.c. of water, 25 c.c. of concentrated sulphuric acid were added, and the whole was boiled. A solution of  $N/2$ -chloride-free potassium permanganate was prepared. A blank test having shown that 43.5 c.c. of this solution were necessary to give a permanent pink colour with the halide mixture used, 43.0 c.c. of permanganate were added slowly to the boiling acidified halide solution, and boiling was continued until all the bromine was removed and the solution became colourless. Ammonium nitrate (10 g.) was dissolved in the solution, which was then cooled and titrated electrometrically with  $N/100$ -silver nitrate. The result was: chloride taken, 0.0050; found, 0.0051 g.

The presence of manganous salts in the titration beaker does not affect the titration adversely in any way. Owing to the presence of sulphuric acid in the solution, it is preferable to add ammonium nitrate or sodium acetate, rather than barium nitrate, for the titration. Although a titration carried out with barium sulphate present gave accurate results, its presence is best avoided if the possibility of occlusion is to be eliminated.

*Estimation of Low Percentages of Bromide in Chloride.*

Although percentages of chloride in bromide from 50% down to 0.2% have been shown capable of accurate estimation, very low percentages of bromide in chloride cannot be accurately determined by direct electrometric titration. It has been found quite impossible, by direct methods of electrometric titration, to determine bromide present to the extent of less than 5% in chloride.

The following observations were made with 5% bromide in chloride of *N*/10-strength: (a) with 20 c.c. of mixture + 150—200 c.c. of 5% ammonium nitrate titrated with *N*/100-silver nitrate, a curve was obtained, with no sign of a sharp break, but merely a slight increase of slope over a long range of c.c. silver nitrate added.

(b) (a) was repeated in presence of saturated ammonium nitrate solution with the same results.

The absence of a sharp break is peculiar. When a mixture of, say, equal proportions of chloride and bromide is titrated, the composition varies until it passes through a stage at which there is 5% bromide in chloride, and yet a sharp bromide end-point is obtained. The only difference between this and the cases (a) and (b) above is that there is a bulk of silver bromide present, owing to precipitation of the first 45% of bromide.

(c) In order to simulate these conditions, 20 c.c. of *N*/10-ammonium bromide were titrated to the end-point with *N*/10-silver nitrate. 20 C.c. of *N*/10-5% bromide in chloride were then added, and the titration was continued with *N*/100-silver nitrate. The same results were found as in (a) and (b). By plotting the curves of (a), (b), and (c) on a more closed scale, a fairly sharp increase of slope was observed in the neighbourhood of the theoretical end-point, but it was impossible to locate the end-point with any degree of certainty.

Titration with *N*/100-silver nitrate is thus useless for determining 5% of bromide in chloride. The only way of obtaining satisfaction seemed to be to work with a higher concentration of silver nitrate, and a bigger bulk of halides.

(d) 10 C.c. of 5% bromide in chloride + 50 c.c. of 5% barium nitrate, titrated with *N*/10-silver nitrate, gave a sharp break at

0.5 c.c. of silver nitrate, the theoretical value. The degree of accuracy to be expected with a titre of 0.5 c.c. is, however, low.

(e) (d) was therefore repeated with 100 c.c. of 5% bromide in chloride. Solid ammonium nitrate was dissolved in this, and it was titrated with  $N/10$ -silver nitrate. A definite break was obtained in the titration curve, and its inflexion point being taken as the bromide end-point, the theoretical bromide value was found. A quotation from Müller has already been cited, in which he states that bromide cannot be accurately determined in presence of chloride, unless the molar concentration of bromide exceeds that of chloride by five times.

As shown above, however, it is possible to estimate 5% bromide in chloride of  $N/10$ -strength by titration of 100 c.c. with  $N/10$ -silver nitrate. Percentages less than 5 cannot be so estimated with any degree of accuracy. The difficulty could probably be overcome by adding a known amount of bromide to adjust the ratio of  $\text{Br}^- : \text{Cl}^-$  to 1 : 1, titrating this mixture, and obtaining the original bromide by difference. The objection to this seems to be that any error in the titration of the total halide would be thrown on to the small percentage of bromide originally present.

Müller ("Elektrometrische Massanalyse," 2nd edn, 1923, p. 95), titrating 5% bromide in chloride directly, got accurate results\* in presence of barium nitrate, but a + 16% error in the bromide in absence of barium nitrate. With a 2.5% bromide in chloride he got an error of + 16% in presence of barium nitrate, and + 36% in absence of added salts. These results have been substantially confirmed in the experiments described here.

To estimate low proportions of bromide in chloride it thus appeared necessary to isolate the bromide as bromine either free from chlorine, or else with such an amount of chlorine as to give a preponderance of bromine, convert the bromine (and chlorine) into bromide (and chloride), and then titrate the bromide electrometrically. The presence of a small amount of chloride from chlorine carried over with the bromine will not be harmful, since, as has been shown, low ratios of chloride in bromide can be readily estimated.

Removal of bromine with bromate in acid solution was first tried. The method was satisfactory for 28.6% bromide in chloride, but for 1% bromide, it gave very variable results, and was therefore abandoned.

The use of permanganate proved to be satisfactory. The apparatus consists of a conical flask fitted with a stopper (preferably

\* This appears from Müller's table (p. 95) to be just a chance accuracy, and is contradictory to a statement by Müller quoted earlier in this paper.



of glass, ground in) carrying a graduated tap funnel for the permanganate, and a tube with a trap, leading to a vertical condenser dipping into ammonia in a receiving flask. The bromide-chloride mixture is put in the conical flask together with plenty of sulphuric acid and boiled. Permanganate is run in drop by drop until the pink colour persists for a short time, and then a further addition of about the same volume of permanganate is made, and the solution is boiled for some time, until it loses its colour. The ammonia in the receiver is acidified, ammonium nitrate added and the solution titrated as usual. The following figures show that this method is capable of a fair degree of accuracy :

Mixture examined.	Bromide in chloride.	
	Theoretical %.	% Found.
200 C.c. of 1% bromide in chloride ( <i>N</i> /10).	1	(1) 0.95
40 C.c. of 0.5% bromide in chloride ( <i>N</i> /10).	0.5	(2) 0.9 0.49

A further attempt to estimate bromide in chloride was made using the method of Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, 45, 623), in which the halides are mixed with potassium cyanide solution and sulphuric acid and titrated electrometrically to the CNBr end-point with permanganate solution. The method was tried with a platinum electrode and calomel cell, but the potential readings were very inconsistent and jerky, and the rate of attainment of equilibrium of potential was very variable. The method of Willard and Fenwick depends on the same reaction as that employed by Müller and Schuch (*Z. Elektrochem.*, 1925, 31, 332) for estimating halogens in solution by electrometric titration with cyanide. Various modifications of this method were tried without success.

The ingenious method of "differential titration" due to Cox, already mentioned, was investigated for the titration of bromide with silver nitrate, and good results were obtained. An example of the method used is as follows : 10 c.c. of *N*/10-bromide + 200 c.c. of water were put into each of two beakers. The solutions were united by a bridge of saturated ammonium nitrate solution, and silver electrodes were immersed one in each solution and connected to the potentiometer. The two solutions were titrated simultaneously with *N*/10-silver nitrate from two burettes, one being kept 0.2 c.c. ahead of the other, the *E.M.F.* being measured after each addition of silver nitrate as usual. A very sharp maximum was obtained, and equilibrium was practically instantaneous. Bromide found = 20.1 c.c.; theoretical = 20.14 c.c. of *N*/10-Ag. The method is thus satisfactory for plain bromide solution. Its advantages are that it eliminates the use of the calomel cell, and

equilibrium is instantaneous at the end-point. Its disadvantage is that manipulation of two burettes is necessary. On the whole, however, it appears to possess no ultimate advantage over the ordinary method.

The differential method was tried for the estimation of 1% bromide in chloride, but without success. At the bromide end-point the curve certainly tended to a maximum, but this could not be definitely located.

#### *Estimation of a Mixture of Three Halides.*

Since a pair of soluble halides can be estimated accurately under certain conditions, it is to be expected that a mixture of three halides could just as accurately be determined under similar conditions.

A mixture containing 3% iodide and 1% chloride in  $N/10$  bromide was examined. This ratio represents possible proportions of halide in a photographic preparation. 20 C.c. of the mixture + 200 c.c. of 5% barium nitrate solution were taken; the bulk was titrated with  $N/10$ -silver nitrate and the end-points were determined with  $N/100$ -silver nitrate. Taken: bromide, 19.48; chloride, 0.23; iodide, 0.59. Found: bromide, 19.48; chloride, 0.22; iodide, 0.59 (the figures denote equivalents of  $N/10$ -silver nitrate).

#### *Analysis of Silver Halides.*

In the analysis of silver halides by electrometric methods, two methods of procedure are possible. The first is to dissolve the silver halides in a suitable solvent and titrate directly the solution obtained. The second method is to set free the halogen from the silver halides in the form of soluble halides, which can be readily titrated by the normal methods.

The only method of the first type known to the author is that due to Müller (*Phot. Ind.*, 1924, 305, 332). The silver halides are dissolved in a slight excess of potassium cyanide solution, and the resulting solution is titrated electrometrically with silver nitrate. The theory of the titration and the method of deducing the results are lucidly described in Müller's original paper. Müller claims satisfactory results in the titration of a single silver halide, and with mixtures of silver iodide with silver bromide or silver chloride. Numerous measurements made to check the accuracy of the method have fully substantiated Müller's claims. The method suffers, however, from a serious limitation in that it does not distinguish between silver bromide and silver chloride. In the analysis of many photographic materials this should be of no account, since the majority of fast plates should consist entirely of silver bromide

and silver iodide mixtures. In the case of some plates, however, chloride is added in addition to the other two halides, and in most cases chloride is present unintentionally because the soluble iodide and bromide used in making the emulsions are rarely, if ever, free from chloride. For the analysis of chloro-bromide emulsions, Müller's method would obviously be unsuitable.

Owing to the limitations of Müller's method, the second type of method, in which the silver halides are converted into soluble halides, was investigated. Samples of pure silver halides were first prepared in the following manner. The preparations were carried out in red light, and the products were stored in dark brown glass bottles.

*Silver chloride* was prepared by adding silver nitrate drop by drop to a vigorously stirred solution of pure potassium chloride until the slightest excess of chloride remained. The precipitate was washed many times with water, and drained by suction. One sample of chloride was dried in a desiccator, but formed such hard lumps that it could not readily be dissolved in cyanide solution. The moist preparation was therefore used.

*Silver bromide* was prepared from a sample of commercial potassium bromide containing about 1% of chloride. It was dissolved in 5% ammonium nitrate solution, and silver nitrate, also in 5% ammonium nitrate solution, was run in drop by drop, the whole being vigorously stirred. Silver nitrate equivalent to 14/17 of the bromide was added during 3 hours. The precipitate was washed five times by decantation, collected, and dried in a desiccator.

*Silver iodide.* Part of the damp sample made for the preparation of pure soluble iodide, as described earlier, was dried in an electric oven at 105°.

### *Conversion of the Silver Halides into Soluble Halides.*

Two methods of reduction of the silver halides to give the halogen in the form of soluble halides were investigated: (a) Direct reduction of the solid silver halide. (b) Reduction of the silver halide in solution.

*Method (a).*—The simplest method of getting the halide in the soluble form is direct reduction of the solid silver salt by a substance such as hydroxylamine. For electrometric titration it is necessary that the excess of the reducing agent be rendered harmless in some simple way which does not involve any loss of halogen.

Destruction of any excess of hydroxylamine could be satisfactorily carried out by gentle ignition with excess of alkali at about 200°. Oxidising agents, which would probably cause loss of halogen, should not be used.

Formic acid was unsuitable as a reducing agent, even on prolonged boiling with the silver salts. Reduction was far from complete, and chocolate-brown products resembling the synthetic photo-halides were formed. Hydroxylamine sulphate in alkaline solution was very efficient, but the reduction of solid silver halides by its means, even on very prolonged stirring, was incomplete in the majority of cases. The spongy silver mass obtained invariably contained traces of unreduced silver halide, which could be detected by dissolving the silver in nitric acid. Attempts were made to peptise the silver halides before reduction and thus render the reduction quantitative. Octyl alcohol was useless for this purpose. Addition of a known excess of potassium iodide gave a finely-divided suspension in the case of silver iodide, but the excess of halogen ions slowed down the rate of reduction so much as to render its use impracticable.

Boiling a suspension of silver iodide in water with zinc and dilute acetic acid gave incomplete reduction.

*Method (b).*—Reduction of the solid halide having proved useless for obtaining quantitative conversion to soluble halide, the reduction of the solution of the silver halides in potassium cyanide solution was investigated. A solution of silver iodide in cyanide was treated with (a) alkaline hydroxylamine, (b) alkaline hydrazine hydrate, (c) sodium hydrosulphite [hyposulphite], and (d) diaminophenol (amidol). With (a) there was no reduction in 18 hours, and with (b) in the same time, only a trace of action. Hydrosulphite reduced the solution directly to silver; and amidol caused reduction on long standing, but there was simultaneous formation of undesirable oxidation products.

When hydrosulphite is added to a solution of silver iodide in cyanide, precipitation of the silver iodide first occurs, and this is followed rapidly by its reduction. If the solutions are too concentrated, coagulation of the silver iodide occurs before it is reduced, and results in a part of the silver halide inside the curds remaining unreduced. Complete reduction of the silver halide can be effected by working in dilute solution, and adding the hydrosulphite solution a little at a time. On each addition a yellow colloidal solution of silver iodide forms. The next addition of hydrosulphite should not be made until reduction of the colloidal suspension due to the previous addition begins.

Attempts were made to prevent coagulation of the silver iodide by adding colloids before reduction. Gelatin and gum arabic effectively prevented coagulation, but their use resulted in the formation of a protected colloidal silver sol on reduction, and this could not be removed by filtration, even after prolonged boiling

with electrolytes. More satisfactory results were obtained with dextrin; the silver formed on reduction with hydrosulphite readily coagulated on boiling, and could be filtered off.

The excess hydrosulphite can be destroyed by boiling with acid, which also removes all the cyanide ions, and the solution of soluble halides is then ready for titration, after addition of barium nitrate or other salt.

Almost all commercial samples of sodium hydrosulphite contain appreciable quantities of chloride. This makes the hydrosulphite method dependent on the ability to obtain the chloride-free product, the application of a correction for chloride being undesirable. Attempts made to prepare pure hydrosulphite as required, *e.g.*, by passing sulphur dioxide gas into water containing metallic zinc, or into a solution of sodium sulphite containing zinc were not satisfactory. Combination of the two operations of preparing hydrosulphite and reducing the silver complex by passing sulphur dioxide into a cyanide solution of silver iodide containing sodium sulphite and metallic zinc did not give very satisfactory results.

*Reduction with Zinc.*—Although hydrosulphite is very satisfactory for reducing the cyanide solution, the difficulty of getting samples free from chloride led to trials with other reducing agents, of which zinc dust or granulated zinc, with acetic acid, proved very satisfactory.

Boiling the solution with granulated zinc and acetic acid gives complete reduction. On adding the acetic acid there is a tendency to form colloidal silver halide, but although in certain cases coagulation sets in, it is not of such a nature as to prevent complete reduction to silver. Addition of sodium acetate to the acetic acid, lowering the acidity to  $p_H$  4.8, did not prevent some silver salt being thrown out of solution.

Results as satisfactory as those obtained with granulated zinc and acetic acid are obtained by boiling with granulated zinc or zinc dust without acid, and no precipitation of silver halide occurs in these cases. It is necessary, however, to add acetic acid after the reduction is over in order to remove the excess of cyanide. The disadvantage in the case of zinc dust is that many samples contain chloride, whereas granulated zinc can be readily obtained very pure.

The conditions for titration of the reduced solution are as follows :

- (1) No free cyanide must be present. This is ensured by boiling with acetic acid.

- (2) Presence of free acetic acid has no adverse effect on the titration of mixed halides. In fact, sodium acetate has been shown to be advantageous.

(3) Undissolved zinc must be filtered off, otherwise further reduction will occur during the titration with silver nitrate.

(4) Zinc ions present in the titration must have no adverse effect. That they do not affect the titration was shown by control titrations to which zinc sulphate had been added.

(5) Boiling a solution of soluble halide with zinc and acetic acid must not result in loss of halogen. Blank experiments showed that no such loss occurred.

The method was then tested quantitatively, with known amounts of standard solutions of silver halides in potassium cyanide. Müller's titration method (*vide supra*) was employed for standardising these solutions. Use of this method for estimating known weights of silver halide in cyanide solution gave very accurate results, and justified its use for the standardisation of solutions. 20 C.c. of the standard solutions of silver iodide, bromide, and chloride were equivalent to 17·20, 27·10, and 7·65 c.c., respectively, of *N*/10-silver nitrate.

Both granulated zinc and zinc dust reduction gave accurate results with all three halides. The method finally used in all cases is illustrated by the following example :

Stock silver iodide-potassium cyanide solution (20 c.c.) was diluted to about 100 c.c. with water and heated, 1—2 g. of granulated zinc in small pieces were added, the solution was boiled vigorously for 10—15 minutes, 50 c.c. of acetic acid (100 c.c. of glacial acid diluted to 1 litre with water) were added, and boiling was continued vigorously until all smell of cyanide had disappeared. The solution was then cooled and decanted through a filter, the metallic residue being carefully washed several times. Ammonium nitrate was added to the combined filtrate and washings to make about 5% concentration, and titration was carried out electrometrically in the manner already described.

The quantities taken and found, expressed as c.c. of *N*/10-silver nitrate, were : silver iodide, 17·20 and 17·20; silver bromide, 27·10 and 27·10, 27·05; silver chloride, 7·65 and 7·65. The conversion of silver halide into soluble halide is thus quantitative. There should therefore be no more difficulty attending the estimation of mixed silver halides than was the case with mixtures of soluble halides already described. For this reason, exhaustive investigation of mixed silver halides was not made. For two mixtures of silver iodide and silver bromide, reduced with zinc and acetic acid, the values, in c.c. of *N*/10-silver nitrate, were : (1) Bromide : taken, 27·10; found, 27·05. Iodide : taken, 4·30; found, 4·30; (2) Bromide : taken, 27·10 found, 27·09. Iodide : taken, 0·43; found, 0·41.

*Analysis of Photographic Emulsions.*

The method described above was applied to the analysis of photographic emulsions.

Preliminary experiments were made to ascertain whether the reduction of silver halides could be satisfactorily carried out in presence of gelatin. A mixture of standard potassium cyanide-silver iodide solution, 100 c.c. of water, and 25 c.c. of 1% gelatin was heated to boiling, granulated zinc and 50 c.c. of 10% acetic acid were added, and the boiling was continued. In  $\frac{1}{2}$  hour very little reduction had occurred, and the silver halide which had been thrown out of solution was carried away from the sphere of reduction by the frothing gelatin. Several hours' boiling had not resulted in complete reduction.

In another case, the emulsion was scraped off a soaked photographic plate into water, which was heated to disperse the gelatin. Cyanide was added to dissolve the silver salts, and the whole was boiled with zinc and acetic acid. After several hours, reduction was again incomplete.

It was obvious that the presence of gelatin was to be avoided. If the emulsion is boiled with nitric acid to destroy the gelatin there is an element of risk involved, in view of the known action of nitric acid in freeing halogen from silver halides. Lehmann and Bolmer (*Phot. Ind.*, 1922, 467, 491) found that cold nitric acid above a concentration of 47%, and hot nitric acid above 5%, converts silver iodide into silver nitrate and iodine. If, however, 5% nitric acid is used for destroying the gelatin, the halide remains in suspension and cannot be filtered. The workers mentioned recommended a mixture of 4% nitric acid in 20% acetic acid for isolating the silver halide. Valenta (*Phot. Korrr.*, 1914, 51, 122; "Photographische Chemie und Chemikalienkunde," I, 2nd edn, 1921, p. 151) used 20% nitric acid for destroying the gelatin. This practice is criticised by Lehmann and Bolmer, and is shown to lead to errors.

It appeared preferable to avoid the use of oxidising acids for the destruction of the gelatin, in the case of plates, at any rate. The method of fixing out the silver halides with cyanide was therefore tried, with success; this has the advantage of eliminating the need for stripping the emulsion.\*

Numerous commercial plates were investigated, to ascertain the best conditions for analysis. With plates of fast, or special rapid

\* If stripping is considered desirable, it can readily be carried out by means of alkaline sodium benzoate, prepared by dissolving benzoic acid in excess of caustic soda solution.

type, one half-plate provides a suitable quantity of material for investigation, but in the case of thinly-coated plates of the process type, two half-plates should be used.

The method of analysis finally adopted for a half-plate is as follows:

The plate is fixed out in a dish with 100 c.c. of *N*/10-potassium cyanide, and washed by soaking (5 minutes) in three changes of 100 c.c. of water. No silver salts can, in general, now be detected in the gelatin film. As a precaution, however, after washing, the plate is spotted with sodium sulphide; the absence of a brown stain indicates freedom from silver salts. The washings and fixing solution are combined, reduced with zinc and acetic acid, and treated as described for the examination of mixed silver salts. *N*/100- or *N*/10-Silver nitrate is used for titration, according to the amount of the particular halide being analysed. Owing to a slight action of the cyanide solution on the gelatin of the plate, a little gelatin sometimes goes into solution, but it only results in a somewhat slower attainment of equilibrium of potential when dilute silver nitrate is used. With *N*/10-silver nitrate, equilibrium is attained at the normal rate.

The following table shows the results obtained in the analysis of a few commercial plates. These plates were of *unknown* composition, and so no check on the results was available.

Plate.	Size.	AgI.	AgBr.	Total halide.	% AgI.
A. Special rapid.	$\frac{1}{4}$	0.41	6.74	7.15	5.73
B. " "	$\frac{1}{4}$	0.47	8.18	8.65	5.44
C. " "	$\frac{1}{2}$	0.52	13.88	14.40	3.61
D. " "	$\frac{1}{2}$	0.55	13.61	14.16	3.88
E. Process.	$\frac{1}{2}$	0.11	9.30	9.41	1.17

Plates A and B were of one brand. It does not follow from this that they are of identical composition, since variations often occur among plates of the same manufacture. Also it is improbable that the total amount of silver halide is identical on both plates. Similar remarks apply to C and D. The values in columns 3, 4, and 5 refer to c.c. of *N*/10-silver nitrate equivalent to the halides.

At the time when these measurements were made, only one emulsion of accurately known composition was available. Duplicate analyses were made of half-plates hand-coated with this emulsion, with the following results:

	AgI.	AgBr.	Total halide.	% AgI.	
				Found.	Theor.
Plate 1 .....	0.81	19.83	20.64	3.92	3.95
Plate 2 .....	0.80	19.57	20.37	3.92	3.95

The method thus appears capable of giving accurate results. It possesses the great advantage of ease and comparative rapidity.



The author wishes to express his gratitude to Dr. T. Slater Price, F.R.S., Director of Research to the British Photographic Research Association, for the interest he has taken in this work, and for the valuable criticism and advice he has given.

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LONDON.

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## CV.—*The Absorption Spectra of Various Derivatives of Salicylic Acid.*

By JOHN EDWARD PURVIS.

THE author described (J., 1925, 127, 2771) the absorption spectra of various compounds derived from salicylic acid in order to compare the influence of different types of nuclei. The investigation has been continued with the following coloured and colourless salts and other compounds of the acid. The substances were examined in the first instance in  $M/200$ -solutions, with the exceptions of 3-nitrosalicylic acid and 5-aminosulphosalicylic acid, which were not so soluble. These were examined in  $M/2000$ - and  $M/20,000$ -solutions.

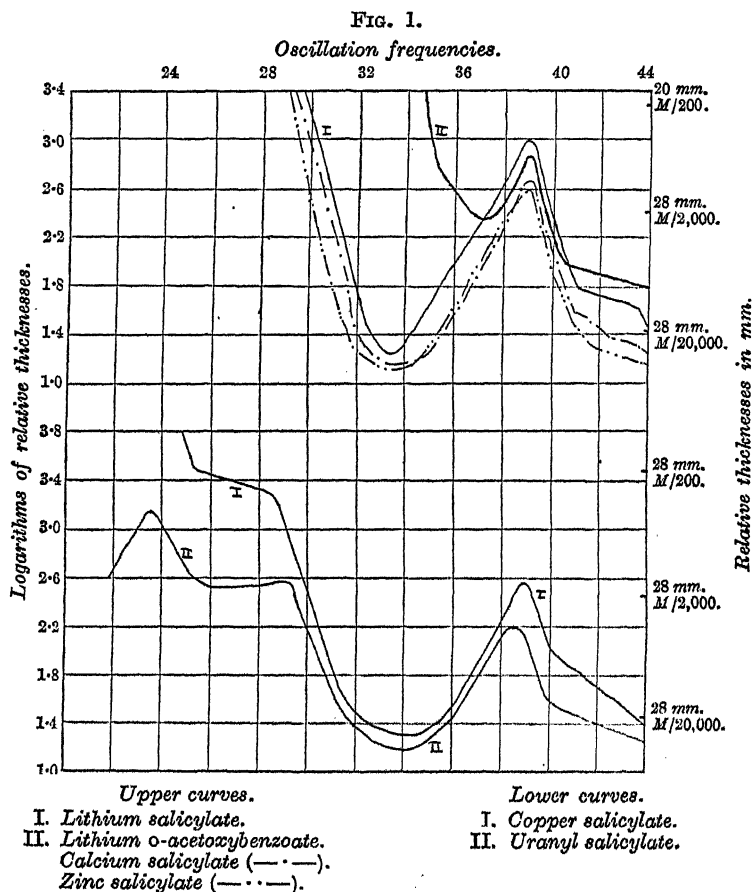
*Lithium, calcium, and zinc salicylates.* The curves (Fig. 1, upper curves) show in the lithium compound a band at  $1/\lambda$  3350 ( $\lambda$  2984) comparable with that of salicylic acid (*loc. cit.*), but the more refrangible band between  $1/\lambda$  4120 ( $\lambda$  2425) and  $1/\lambda$  4300 ( $\lambda$  2320) is not so well marked as that in salicylic acid. In the calcium and zinc salts, somewhat similar phenomena were noticed; and there are differences in the positions of the bands dependent on the respective molecular weight. The less refrangible band of the monobasic lithium salt is not, of course, so strong as that of the calcium and zinc salts.

*Lithium o-acetoxybenzoate* (Fig. 1, upper curves). The replacement of the hydroxyl hydrogen atom by the acetyl group has produced a similar change to that in salicylic acid and *o*-acetoxybenzoic acid, and in theobromine salicylate and theobromine *o*-acetoxybenzoate (*loc. cit.*). The less refrangible band at  $1/\lambda$  3740 ( $\lambda$  2672) is very weak and is shifted towards the more refrangible regions; and the more refrangible band is represented by a more rapid extension of the rays from about  $1/\lambda$  4020 ( $\lambda$  2486). As the author has previously pointed out in the case of *o*-acetoxybenzoic acid, this has produced an absorption comparable with that of benzoic acid.

*Copper salicylate* (bluish-green). The curve (Fig. 1, lower curves)

shows the less refrangible band of salicylic acid well developed, and the more refrangible one is nearly obliterated. There is a rapid absorption of the rays between about  $1/\lambda$  2850 ( $\lambda$  3506) and  $1/\lambda$  2550 ( $\lambda$  3919), extending well into the visible region.

*Uranyl salicylate* (reddish-brown). The curve (Fig. 1, lower curves) has a somewhat similar form to that of copper salicylate,

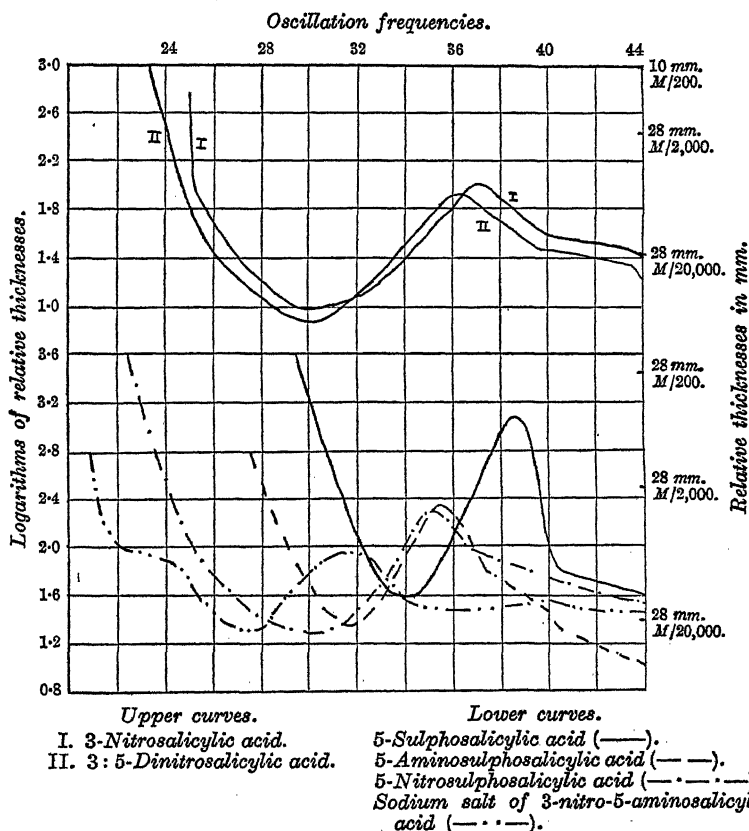


but the band between  $1/\lambda$  2940 ( $\lambda$  3400) and  $1/\lambda$  2520 ( $\lambda$  3967) is better marked, and there is another band on the less refrangible visible parts at about  $1/\lambda$  2200 ( $\lambda$  4544). The band at  $1/\lambda$  3400 ( $\lambda$  2940) is wider than the corresponding band of the copper salt.

*3-Nitrosalicylic acid* (yellow), *3:5-dinitrosalicylic acid* (yellow). In each of these substances there is a large band extending into the visible region (Fig. 2, upper curves), and it is much wider than

the corresponding bands of the substances described above. The more refrangible band is merely indicated by the more rapid extension of the rays from  $1/\lambda$  4000 ( $\lambda$  2498) to  $1/\lambda$  4400 ( $\lambda$  2271) in the nitro-compound, and from  $1/\lambda$  3920 ( $\lambda$  2550) to  $1/\lambda$  4350 ( $\lambda$  2298) in the dinitro-compound. These results are not unlike those described by the author (J., 1915, 107, 966) in the case of some nitro-compounds of benzoic and cinnamic acids.

FIG. 2.



5-Sulphosalicylic acid, 5-aminosulphosalicylic acid. These two substances show (Fig. 2, lower curves) that the more refrangible band of salicylic acid is not so definite, but in each case the less refrangible one is well marked. In the amino-compound this band is not quite so strong as it is in the sulpho-compound, and there are differences in the persistency.

5-Nitrosulphosalicylic acid (yellow). There is a wide band

(Fig. 2, lower curves) at  $1/\lambda$  3000 ( $\lambda$  3344) not unlike that of the other nitro-compounds, and extending into the visible region. The more refrangible one almost disappears.

*Sodium 3-nitro-5-aminosalicylate* (reddish-brown). This substance (Fig. 2, lower curves) exhibits a large band at  $1/\lambda$  2750 ( $\lambda$  3633) which extends rapidly into the visible regions. This band may be compared with that of the other nitro-compounds. There is also a shallow band from about  $1/\lambda$  3400 ( $\lambda$  2939) to  $1/\lambda$  3930 ( $\lambda$  2543).

*Hexamethylenetetramine*, *Hexamethylenetetramine salicylate*. Through 56 mm. thickness of a  $M/200$ -solution hexamethylenetetramine exhibited no band; and the rays were transmitted to  $\lambda$  2150. Its salicylate, on the other hand, exhibited an absorption band comparable with that of salicylic acid. Paraldehyde shows no specific absorption (J., 1925, 127, 9); and it is suggested that, like paraldehyde, the condensation of formaldehyde with ammonia in the production of hexamethylenetetramine neutralises the free valencies of the aldehydic oxygen which produce a band in formaldehyde itself.

*Results.*—Considering these results with those of salicylic acid and its various salts (*loc. cit.*), it appears that the specific absorption of the substances depends on the nature of the basic and of the acid radicals. Changes in the nature of the one or the other produce changes in the position and intensity of the bands characteristic of each. The author has already shown, in a study of the absorption spectra of some organic and inorganic salts of didymium (*Proc. Camb. Phil. Soc.*, 1923, 21, 781), that the bands of didymium in the visible regions were modified in intensity according to the type of the negative radical united with this base.

As regards the other derivatives of salicylic acid, the influence of the nitro-group in the benzene radical powerfully intensifies and shifts the less refrangible band of the acid, but appears to lessen that of the more refrangible one. Also the replacement of the hydrogen atom of the hydroxyl group by a radical, as in lithium salicylate and lithium *o*-acetoxybenzoate, changes the absorption capacity of the other parts of the molecule; and this is comparable with the phenomena of *o*-acetoxybenzoic acid, and of the *o*-acetoxybenzoates of theobromine and quinine.

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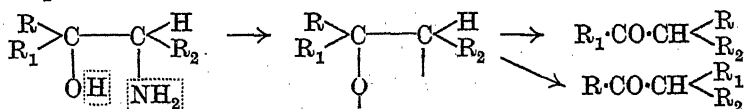
[Received, January 8th, 1926.]

CVI.—*Elimination of the Amino-group of Tertiary Amino-alcohols. Part III. A New Method for the Preparation of Optically Active Ketones.*

By ALEX. MCKENZIE, ROBERT ROGER, and GEORGE OGILVIE WILLS.

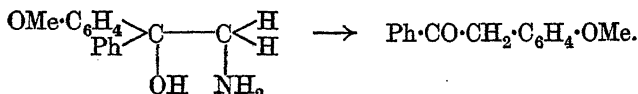
PREVIOUS research (McKenzie and Richardson, J., 1923, **123**, 79; McKenzie and Roger, J., 1924, **125**, 844; McKenzie and Dennler, J., 1924, **125**, 2105; McKenzie and Wills, J., 1925, **127**, 283) carried out in this laboratory on the behaviour of certain tertiary amino-alcohols towards nitrous acid has demonstrated that in no case was the glycol corresponding with the amino-alcohol isolated, although such glycols are readily enough accessible in other ways. The action is thus an abnormal one, the product invariably being a ketone (a dehydration product of the glycol). At once the simplest and the most obvious interpretation would be based on the assumption that the glycol is formed as an intermediate phase and then undergoes dehydration. This is an assumption which is, however, untenable, and the experimental evidence is conclusive in proving that a hydrocarbon residue migrates from one carbon atom to another adjacent to it. A process, such as this, for effecting the migration of groups was designated by McKenzie and Roger as "semipinacolinic deamination" from its analogy with the semipinacolinic changes which have come under the observation of Tiffeneau, Orékhov, and their colleagues.

The latter chemists, as well as Meerwein, have studied the dehydration of glycols where the two hydroxyl groups are bound to contiguous carbon atoms by gripping forces which vary in intensity. Wherever the variation of this gripping force is very great, that is to say, when the one hydroxyl group is very firmly and the other very loosely bound, the investigation of the dehydration of a glycol does occasionally provide a good indication of the migrational aptitude of groups. But, especially in other cases, semipinacolinic deamination is proving of service where the evidence deduced from the dehydration of glycols as to migrational aptitude is rather inconclusive. In fact, the method possesses the advantage of being a general one for testing the migrational aptitude of groups, as the elimination of the amino-group necessarily involves group transposition :

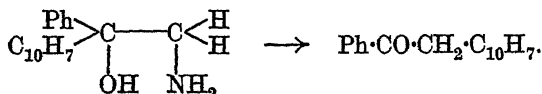


An extension of the method has lately been published by Orékhov

and Roger (*Compt. rend.*, 1925, **180**, 70) to embrace tertiary amino-alcohols where the amino-group is attached to a secondary carbon atom. Thus, the action of nitrous acid on  $\beta$ -hydroxy- $\beta\beta$ -diphenylethylamine leads to the formation of deoxybenzoin and not of *as*-diphenylethylene oxide, whilst the interpretation advanced by us agrees with that of Orékhov and Roger. Again, the superiority of the migrational aptitude of the *p*-anisyl as compared with the phenyl group is shown by the formation of *p*-methoxydeoxybenzoin from  $\beta$ -hydroxy- $\beta$ -phenyl- $\beta$ -anisylethylamine:

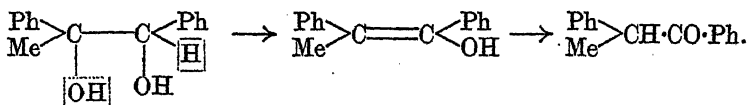


Further, when  $\beta$ -phenyl- $\beta$ -( $\alpha$ )-naphthylethylamine is deaminated (Luce, *Compt. rend.*, 1925, **180**, 145), the naphthyl group wanders more readily than does the phenyl group, since  $\omega$ - $\alpha$ -naphthyl-acetophenone is formed:



In the present paper, an application of our method to optically active amino-alcohols is described. The products are ketones, and it is remarkable that *optical activity is preserved in spite of the molecular rearrangement which is involved*.

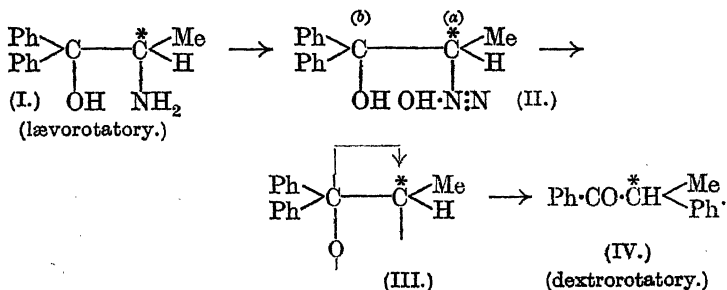
It may be recalled that in the formation of diphenylacetone from  $\beta$ -hydroxy- $\alpha\beta$ -diphenylpropylamine a phenyl group migrates from a carbon atom to the adjacent one to which a phenyl group is already attached, and it would not therefore be anticipated (since diphenylacetone does not possess an asymmetric carbon atom) that the resulting ketone would be optically active if the starting point were the optically active amino-alcohol. The action of concentrated sulphuric acid on methylhydrobenzoin, the glycol corresponding with the above amino-alcohol, forms a striking contrast to the above, inasmuch as there is no group wandering, the change being what Tiffeneau calls "vinyl dehydration":



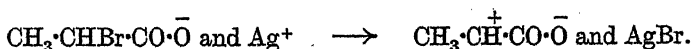
Now when the dextrorotatory methylhydrobenzoin, obtained by acting on *l*-benzoin with magnesium methyl iodide, is dehydrated with concentrated sulphuric acid, the resulting methyldeoxybenzoin is optically inactive, as it would necessarily be if the mechanism of

the action were that of vinyl dehydration. But McKenzie and Roger (J., 1924, 125, 2148) have shown that, when the dehydrating agent is dilute sulphuric acid, the optical activity does not disappear; the product is not, however, an optically active methyldeoxybenzoin, but the lævorotatory diethylenic oxide,  $\left(\text{CPhMe}\cdot\text{CHPh}\right)_2$ . It is possible that the *r*-methyldeoxybenzoin, which is formed when concentrated sulphuric acid is employed, is produced from the lævorotatory diethylenic oxide formed as an intermediate phase, whilst racemisation accompanies the transformation of the oxide into the *r*-ketone.

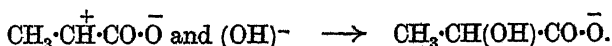
In the experimental section, the preparation of *d*-methyldeoxybenzoin is described. *d*-Alanine was converted into its ethyl ester hydrochloride, from which 1-β-amino-α-diphenyl-*n*-propyl alcohol was obtained by the action of magnesium phenyl bromide.\* When the amino-alcohol, with  $[\alpha]_D - 82^\circ$  in chloroform, is acted on by nitrous acid, it gives the *d*-ketone with  $[\alpha]_D + 207^\circ$  in the same solvent. On the interpretation of semipinacolic deamination, the following mechanism is suggested:



In a discussion of the Walden inversion, Büllmann (*Annalen*, 1912, 388, 330) depicts the action of silver nitrate on α-bromopropionic acid as taking place between the silver ion and the acid ion on the lines:



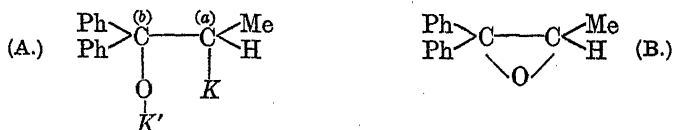
The resulting "Zwitterion" then combines with the hydroxyl ion from water:



\* The designations *d*- and *l*- throughout this paper mean dextrorotatory and lævorotatory, respectively, and do not refer to configurative relationships. The dextrorotatory alanine is converted in the above case into a lævorotatory amino-alcohol which is, however, configuratively related to the parent amino-acid.

Biilmann advanced this idea as a basis of some generalisations which are untenable, as they were framed on an imperfect recognition of the literature and were not in accordance with the experimental facts. McKenzie and Clough (J., 1913, **103**, 687), in their criticism of Biilmann's paper, pointed out that since a "Zwitterion" is supposed to be electrically neutral, it cannot even be urged that a free electric charge plays the part of the fourth grouping which is necessary for the retention of asymmetry. At the same time, the conclusion was drawn that if Biilmann's idea were accepted, the formation of an optically active structure containing a tervalent carbon atom must be admitted, a view for which there was not the slightest experimental evidence.

It might be submitted that such evidence is now forthcoming in the retention of asymmetry during the formation of *d*-methyldeoxybenzoin (IV) from *l*- $\beta$ -amino- $\alpha\alpha$ -diphenyl-*n*-propyl alcohol (I). Various interpretations could be advanced, and of these the one which we favour as being the least unsatisfactory is the following. After the elimination of the nitrogen from (II), the carbon atom (*a*), from which the nitrogen has been detached, retains an electric charge *K*; the oxygen atom attached to the contiguous carbon atom (*b*) also retains an electric charge *K'*, so that (III) would be written thus (A) :



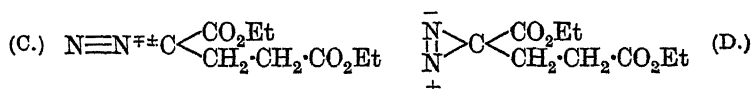
Were those charges of opposite kinds, positive and negative, the formation of diphenylpropylene oxide (B) would have been anticipated instead of that of the isomeric methyldeoxybenzoin. Now diphenylpropylene oxide (Stoermer, *Ber.*, 1906, **39**, 2288) is a stable compound, which under the experimental conditions adopted would have been isolated if it had been formed. Since it is not formed, the assumption—a very problematical one—is made that the electric charges as pictured above are of the same sign, and repel one another. During the transposition of a phenyl group to carbon atom (*a*), we are dealing with a reaction of substitution, the charge *K* playing the part of a group and being displaced by a phenyl group which may or may not occupy the position vacated by the amino-group, so that on this picture a *Walden inversion* is possible within the molecule itself.

There is no evidence available as to whether *d*-methyldeoxybenzoin has the same configuration as the *d*-alanine from which it is prepared; so far as is known, it may equally well have the



opposite configuration. Now one of us in the course of work on the Walden inversion has shown that displacement racemisation very frequently accompanies the displacement of groups in optically active compounds, especially in such as have a phenyl group attached to the asymmetric carbon atom, and it is thus rather significant that the crude product from the deamination of the *l*-amino-alcohol gave a value for its specific rotation which is considerably below that of the optically pure ketone (see experimental part). In this product we probably had to deal with a mixture of the *r*- and *d*-ketones, from which the latter was easily isolated by repeated crystallisation.

There are several examples on record where an electric charge is put forward as playing the part of a group in retaining asymmetry. For example, Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2259) point out that the electronic formula for an aliphatic diazo-compound suggests the possibility of such a compound exhibiting optical activity, although this is not apparent from the formulæ either of Curtius or of Angeli and Thiele. Chiles and Noyes (*J. Amer. Chem. Soc.*, 1922, **44**, 1798) claim to have obtained several optically active aliphatic diazo-compounds which do not contain an asymmetric atom in the old sense of the term, thus diethyl diazoglutarate is formulated as (C) on the basis of the Angeli-Thiele scheme,

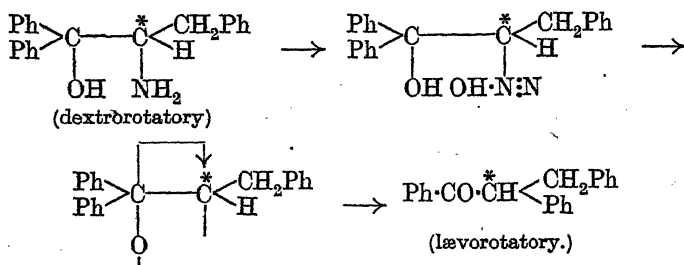


which is in better agreement with the modern views of Lewis and Langmuir than is (D) on the Curtius scheme. Further observations by Levene and Mikeska (*J. Biol. Chem.*, 1922, **52**, 485; 1923, **55**, 795) on diethyl diazosuccinate indicate that a compound of the type  $\text{N}_2 = \text{C} \begin{array}{l} \text{R}_1 \\ \text{R}_2 \end{array}$  can exhibit optical activity, whilst Phillips (*J.*, 1925, **127**, 2552) has described an optically active form of ethyl *p*-toluenesulphinate,  $\text{EtO} \cdot \text{S}^+(\bar{\text{O}}) \cdot \text{C}_6\text{H}_4$ . In a recent historical survey (*Die Naturwissenschaften*, 1925, 331) Walden has also directed attention to the asymmetry of the sulphur, selenium, and tin compounds prepared by Pope, and suggests that the sulphur atom in the optically active methylethylthetine ion,  $\text{CH}_3 > \text{S} \begin{array}{l} \text{CH}_2 \cdot \text{CO}_2\text{H} \\ \text{C}_2\text{H}_5 \end{array}$ ,

for example, has an electric charge which plays the part of a group.

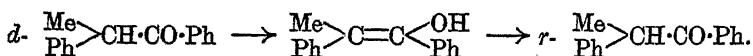
Other examples of the application of semipinacolinic deamination for the preparation of optically active ketones are now described. Whereas *d*-alanine gives, by the action of magnesium phenyl bromide on its ester hydrochloride, an amino-alcohol of the opposite

sign of rotation, the amino-alcohol obtained from *d*-phenylalanine by the same method has the same sign of rotation as that of the parent amino-acid, namely, dextrorotatory, and it has the same configuration. The deamination, however, caused a change of sign, *d*- $\beta$ -amino- $\alpha$ -diphenyl- $\beta$ -benzylethyl alcohol giving *l*-benzyldeoxybenzoin:



Thus, whilst dextrorotatory alanine gives dextrorotatory methyldeoxybenzoin, the ketone derived from dextrorotatory phenylalanine is laevorotatory. In a similar manner, *l*-phenylalanine was converted into a laevorotatory amino-alcohol which gave *d*-benzyldeoxybenzoin. The configuration of the *d*- and *l*-benzyldeoxybenzoins in relationship to the parent amino-acids is unknown owing to the possibility of an intramolecular Walden inversion during the deamination of the amino-alcohol.

The optically active ketones described are very readily racemised at the ordinary temperature when a few drops of alcoholic potash are added to their alcoholic solutions. For comparison, the effect of the catalyst on *l*-benzoin is described. The catalytic racemisation of *l*-benzoin was first interpreted by Wren (J., 1909, 95, 1593) on the basis of a desmotropic change caused by the migration of a hydrogen atom, and on this assumption *d*-methyldeoxybenzoin undergoes racemisation through an enolic complex:



Subsequent work by McKenzie and Wren on the hydrolysis of optically active esters by alcoholic potash (compare McKenzie and Smith, *Ber.*, 1925, 58, 894) and by McKenzie and Smith on the catalytic racemisation of optically active acid amides (J., 1922, 121, 1348) has provided evidence that the catalyst is potassium ethoxide, and it is suggested that the hypothetical enolic isomeride is formed only after the catalyst has combined with the ester or amide. A similar interpretation can be advanced with regard to ketones like methyldeoxybenzoin which contain (a) a phenyl group attached to the asymmetric carbon atom, and also (b) a hydrogen

atom attached to the asymmetric carbon atom which in turn is attached directly to a carbonyl group. The point is emphasised that the latter hydrogen atom has no migrational tendency in the ketone itself, and does not become mobile until an additive complex with potassium ethoxide has first been formed.

We are continuing our work on semipinacolinic deamination, more particularly with reference to the preparation of optically active ketones derived from phenylaminoacetic acid, phenylalanine and alanine. A few additional observations on the action of magnesium benzyl chloride on *d*-benzyldeoxybenzoin, ethyl *r*-alanine hydrochloride, and ethyl *r*-phenylaminoacetate hydrochloride, respectively, and on the deamination of *r*- $\beta$ -amino- $\beta$ -phenyl- $\alpha$ -dibenzylethyl alcohol are recorded at the end of the experimental section.

## EXPERIMENTAL.

### *Optically Active Methyldeoxybenzoin.*

*Action of Magnesium Phenyl Bromide on Ethyl d-Alanine Hydrochloride.*—The final purification of the *d*-alanine employed was effected by dissolving the amino-acid in hot water, and then adding rectified spirit until crystallisation started. The amino-acid separated in long, silky needles, and, for comparison with the value of the specific rotation quoted by Fischer (*Ber.*, 1906, **39**, 464), 0.8000 g. was made up to 10 c.c. with *N*-hydrochloric acid; this solution gave  $\alpha_D + 1.17^\circ$  in a 1-dm. tube, whence  $[\alpha]_D + 10.4^\circ$  for the hydrochloride ( $c = 11.276$ ), a value identical with Fischer's.

*d*-Alanine ethyl ester hydrochloride (15 g., 1 mol.) was added in instalments to an ethereal solution of magnesium phenyl bromide prepared from bromobenzene (150 g., 10 mols.), and the mixture was heated for 5 hours. The additive complex underwent slow decomposition when ice, ammonium chloride, and ammonia were added. When the decomposition was completed, the mixture was extracted several times with ether, the ethereal solution was dried with anhydrous sodium sulphate, the ether was expelled, and the resulting oil recrystallised from light petroleum. The crystals obtained were washed with light petroleum, and then consisted of the optically pure amino-alcohol (5.8 g.). The light petroleum was evaporated from the filtrates, the diphenyl was removed by distillation in steam, and the residual oil was extracted with ether. The oil resulting from the ethereal solution was dissolved in hot aqueous alcohol, and a mixture of oil and crystals separated on cooling. The oil was separated from the crystals by means of light petroleum, and in this manner an additional 5.2 g. of the amino-alcohol were obtained. Total yield = 11 g.

In another preparation the procedure was varied as follows. *d*-Alanine ethyl ester hydrochloride (8 g.) was added gradually to the Grignard reagent prepared from bromobenzene (98 g.), and the mixture after 3 hours' heating was decomposed by ice and dilute hydrochloric acid. In this case the diphenyl remained in the ethereal layer, which was separated from the aqueous layer containing the solution of the hydrochloride of the amino-alcohol. The latter solution was then decomposed by ammonia, but the precipitate which formed contained, not only the free amino-alcohol, but also some of its hydrochloride; the latter was removed by treatment with hot water. Yield of pure amino-alcohol = 4 g. The homogeneity of the amino-alcohol from this and from the preceding preparation was established by repeatedly crystallising from aqueous alcohol and examining the crystals polarimetrically. The amino-alcohol prepared from *d*-alanine is laevorotatory in chloroform, or in ethyl alcohol.

1- $\beta$ -Amino- $\alpha$ -diphenyl-*n*-propyl alcohol,  $\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CPh}_2\cdot\text{OH}$ , separates from aqueous alcohol in needles, m. p. 101.5–102.5°. The *r*-isomeride (McKenzie and Wills, *loc. cit.*) also melts at 101.5–102.5°. The *l*-amino-alcohol is very sparingly soluble in water or in light petroleum, and readily soluble in ethyl alcohol, chloroform, benzene, toluene, or acetone (Found: C, 79.1; H, 7.7.  $\text{C}_{15}\text{H}_{17}\text{ON}$  requires C, 79.3; H, 7.5%). Its colour reaction with concentrated sulphuric acid is similar to that exhibited by the *r*-isomeride. Its specific rotation was determined in chloroform:  $l = 2$ ,  $c = 1.6776$ ,  $\alpha_D^{15^\circ} = -2.76^\circ$ ,  $[\alpha]_D^{15^\circ} = -82.3^\circ$ ;  $\alpha_D^{15^\circ} = -3.32^\circ$ ,  $[\alpha]_D^{15^\circ} = -99.0^\circ$ . In ethyl alcohol:  $l = 2$ ,  $c = 1.6628$ ,  $\alpha_D^{15^\circ} = -2.11^\circ$ ,  $[\alpha]_D^{15^\circ} = -63.4^\circ$ ;  $\alpha_D^{15^\circ} = -2.51^\circ$ ,  $[\alpha]_D^{15^\circ} = -75.5^\circ$ .

*The Action of Nitrous Acid on 1- $\beta$ -Amino- $\alpha$ -diphenyl-*n*-propyl Alcohol.*—A solution of sodium nitrite (2 g.) in water (10 c.c.) was added drop by drop in the course of  $\frac{3}{4}$  hour to 2.2 g. of the amino-alcohol dissolved in 75 c.c. of 25% acetic acid, the temperature being kept at 0° during the addition. The whole was kept at 0° for 5 hours. The oil, which at first separated, crystallised slowly in needles, which were collected, washed with water, and as usual dried in a vacuum over sulphuric acid before a polarimetric determination was made. Yield: 1.9 g. In chloroform:  $l = 2$ ,  $c = 2.0092$ ,  $\alpha_D^{15^\circ} + 6.33^\circ$ ,  $[\alpha]_D^{15^\circ} + 158^\circ$ . Thus the laevorotatory amino-alcohol gave a dextrorotatory ketone. After one crystallisation of the product from aqueous alcohol, fine, silky needles were obtained giving the following value in chloroform:  $l = 2$ ,  $c = 2.0096$ ,  $\alpha_D^{15^\circ} + 7.15^\circ$ ,  $[\alpha]_D^{15^\circ} + 178^\circ$ . As the substance, however, was not yet optically pure, the deamination of the amino-alcohol was conducted in three additional experiments with 2.5 g., 4.3 g.,

and 5.2 g., respectively. The 9 g. of crude ketone thus obtained were crystallised repeatedly from aqueous alcohol until determinations of the rotatory power showed that the ketone had been obtained pure. Five crystallisations were necessary. Yield = 4 g.

*d*-Methyldeoxybenzoin,  $C_6H_5 \cdot CH(CH_3) \cdot CO \cdot C_6H_5$ , crystallises from aqueous alcohol in glistening, silky plates or needles, m. p. 34–35° (Found: C, 85.5; H, 6.7.  $C_{15}H_{14}O$  requires C, 85.7; H, 6.7%). It is readily soluble in the commoner organic solvents. It gives a pale yellowish-green coloration when a trace is dissolved in cold concentrated sulphuric acid. Determinations of its specific rotation gave the following results. In chloroform for  $c = 1.0715$  ( $l = 2$ ):

$\lambda$ .....	6563	5893	5461	4861	4358
$\alpha_D^{17}$ .....	+3.39°	+4.44°	+5.57°	+7.99°	+11.86°
$[\alpha]_D^{17}$ .....	+158°	+207°	+260°	+373°	+553°

In ethyl alcohol:

$$l = 2, c = 2.2320, \alpha_D^{18} + 9.41^\circ, [\alpha]_D^{18} + 210.8^\circ.$$

After 1 day at the ordinary temperature, the solutions exhibited no autoracemisation.

#### *Optically Active Benzyldeoxybenzoins.*

*Resolution of r-Phenylalanine.*—The method of Fischer and Schoeller (*Annalen*, 1907, 357, 1) was employed. Formyl-*r*-phenylalanine was resolved by brucine in methyl-alcoholic solution, and the resulting *d*- and *l*-formyl-acids were hydrolysed by hydrobromic acid. The *d*-phenylalanine obtained gave in aqueous solution:  $l = 2, c = 2.043, \alpha_D^{16} + 1.43^\circ, [\alpha]_D^{16} + 35.0^\circ$ , whilst the *l*-amino-acid gave in the same solvent:  $l = 2, c = 2.043, \alpha_D - 1.42^\circ, [\alpha]_D - 34.8^\circ$ . The values quoted by Fischer and Schoeller are: for the *d*-acid,  $[\alpha]_D^{20} + 35.14^\circ$ , and for the *l*-acid,  $[\alpha]_D - 35.09^\circ$ .

For the preparation of the optically active phenylaminoacetic acids, the resolution of the *r*-acid by Reyhler's *d*-camphorsulphonic acid\* was in our experience (McKenzie and Wills, *loc. cit.*) more practicable than that described by Fischer and Weichhold (*Ber.*, 1908, 41, 1286) through the agency of the formyl-*r*-acid. Accordingly, attempts were made to prepare the optically active phenylalanines on similar lines. The homogeneous *dAdB* salt was obtained by combining the *r*-amino-acid with an equimolecular quantity of *d*-camphorsulphonic acid, and then crystallising the salt several times until the rotation was constant in value.

*d*-Phenylalanine *d*-camphorsulphonate separates from water in

\* Recent work on the constitution of Reyhler's acid indicates that the sulphonic group occupies the 10-position in the camphor molecule with sulphonation of the methyl group (Wedekind, Schenk, and Stüsser, *Ber.*, 1923, 56, 633).

needles. In aqueous solution:  $l = 2$ ,  $c = 2.0200$ ,  $\alpha_D^{25} + 0.74^\circ$ ,  $[\alpha]_D^{25} + 18.3^\circ$ . We did not, however, find that this was a convenient method for effecting the resolution. Crystallisation took place too sluggishly, whether effected from water, benzene, aqueous alcohol or aqueous acetone, and the yield of the pure salt was small.

The enantiomorphous salt was prepared by combining *l*-phenylalanine with *l*-camphorsulphonic acid in methyl-alcoholic solution.

*l*-Phenylalanine *l*-camphorsulphonate separates from methyl alcohol in plates, m. p. 109—110°. In aqueous solution:  $l = 2$ ,  $c = 2.0208$ ,  $\alpha_D^{25} - 0.74^\circ$ ,  $[\alpha]_D^{25} - 18.3^\circ$ .

*The Action of Nitrous Acid on l-β-Amino-α-diphenyl-β-benzyl-ethyl Alcohol.*—The *l*-amino-alcohol was prepared by the action of magnesium phenyl bromide on *l*-phenylalanine (compare the preparation of the *d*-amino-alcohol, McKenzie and Wills, *loc. cit.*). The mixture of 1.9 g. of the *l*-amino-alcohol and 40 c.c. of 25% acetic acid was warmed until most of the solid had dissolved, and was then cooled to 0°. The gradual addition of a solution of sodium nitrite (1.3 g. in 10 c.c. of water) during 30 minutes caused the separation of a voluminous solid, which was kept for 4 hours at 0° in contact with the solution. This solid (1.25 g.) was strongly *dextrorotatory*, giving in chloroform solution  $[\alpha]_D + 233^\circ$  for  $c = 1.346$  ( $l = 2$ ). It consisted of the almost pure ketone, and was recrystallised twice from ethyl alcohol.

*d*-Benzyldeoxybenzoin,  $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{Ph}$ , is sparingly soluble in ethyl alcohol, from which it separates in silky needles, m. p. 121—121.5° (Found: C, 88.3; H, 6.5.  $\text{C}_{21}\text{H}_{18}\text{O}$  requires C, 88.1; H, 6.3%). It is readily soluble in chloroform, ether, or acetone. Its specific rotation was determined in chloroform:  $l = 2$ ,  $c = 1.348$ ,  $\alpha_D^{25} + 6.50^\circ$ ,  $[\alpha]_D^{25} + 241^\circ$ . In ethyl alcohol:  $l = 2$ ,  $c = 0.392$ ,  $\alpha_D^{25} + 1.90^\circ$ .

*The Action of Nitrous Acid on d-β-Amino-α-diphenyl-β-benzyl-ethyl Alcohol.*—The deamination was conducted as in the preceding case. The crude product (0.8 g.) obtained from the *d*-amino-alcohol (0.9 g.) was strongly *levorotatory* in chloroform solution, giving  $[\alpha]_D - 195^\circ$  for  $c = 1.5984$  ( $l = 2$ ). It was crystallised thrice from ethyl alcohol until the optically pure ketone was obtained.

*l*-Benzyldeoxybenzoin crystallises from ethyl alcohol in silky needles, m. p. 121—121.5°. With concentrated sulphuric acid, a trace of the compound gives a faint greenish-yellow coloration. The following determinations of the specific rotation were made. In chloroform:  $l = 1$ ,  $c = 1.258$ ,  $\alpha_D^{25} - 3.04^\circ$ ,  $[\alpha]_D^{25} - 242^\circ$ . In acetone:  $l = 1$ ,  $c = 1.118$ ,  $\alpha_D^{25} - 2.45^\circ$ ,  $[\alpha]_D^{25} - 219^\circ$ ;  $\alpha_{461}^{17} - 3.00^\circ$ ,  $[\alpha]_{461}^{17} - 268^\circ$ .

It is very unusual to find an optically active compound and

its inactive isomeride melting at practically the same temperature. Several such cases have been noted in the course of the present research; thus, *r*- $\beta$ -amino- $\alpha\alpha$ -diphenyl- $\beta$ -benzylethyl alcohol melts at 144.5—145.5° (McKenzie and Richardson, J., 1923, **123**, 91), whereas the *d*-isomeride melts at 143—144° (McKenzie and Wills, *loc. cit.*, p. 293). *r*-Benzyldeoxybenzoin melts at 121.5—122° (McKenzie and Richardson, *loc. cit.*; McKenzie and Roger, J., 1924, **125**, 849), whereas the optically active isomerides melt at 121—121.5°, and reference has been already made to *l*- and *r*- $\beta$ -amino- $\alpha\alpha$ -diphenyl-*n*-propyl alcohols, which melt at 101.5—102.5°.

*Catalytic Racemisation of Optically Active Ketones.*

*l*-Benzoin.—This ketone was prepared by the action of magnesium phenyl bromide on *l*-mandelamide (McKenzie and Wren, J., 1908, **93**, 309). A determination was made of its specific rotation in ethyl-alcoholic solution:  $l = 2$ ,  $c = 1.1550$ ,  $\alpha_D^{18} - 3.06^\circ$ ,  $[\alpha]_D^{18} - 132.5^\circ$ . To this solution in a 2-dcm. tube, four drops of ethyl-alcoholic potash (0.4487*N*) were added, and quickly mixed. Polarimetric readings were taken at intervals, and after 1 hour three additional drops of the alcoholic alkali were added. The initial reading immediately after the addition of the alkali was  $\alpha_D - 3.05^\circ$ ;  $t$  = interval (minutes) after addition of the catalyst, and  $\theta^\circ$  = observed angle:

$t$ .....	15	30	45	60	65	80	100	120	140
$\theta^\circ$ ...	-2.77	-2.68	-2.61	-2.61	-2.49	-2.26	-2.00	-1.82	-1.72
$t$ .....	180	220	250	280	340	400	23 hrs.	31 hrs.	5 days
$\theta^\circ$ ...	-1.48	-1.22	-1.06	-0.91	-0.70	-0.55	-0.24	-0.22	-0.22

*d*-Methyldeoxybenzoin.—An ethyl-alcoholic solution of the ketone ( $c = 0.8095$ ) gave  $\alpha_D^{18} + 3.37^\circ$  in a 2-dcm. tube. Four drops of ethyl-alcoholic potash (0.4487*N*) were mixed with the solution, and the fall in rotation was noted as below:

$t$ (mins.) .....	1	10	20	30	40	50	60	90
$\theta^\circ$ .....	+3.36	+3.25	+3.13	+3.04	+2.94	+2.83	+2.74	+2.54
$t$ (hours) .....	2	3	4	5	6	7	7½	23½
$\theta^\circ$ .....	+2.32	+2.00	+1.70	+1.49	+1.25	+1.04	+0.94	+0.10
								+0.07
								+0.00

The alcohol was evaporated from the solution, and the solid was crystallised from ethyl alcohol; silky needles of *r*-methyldeoxybenzoin, m. p. 49.5—50.5°, separated.

*d*-Benzyldeoxybenzoin.—An ethyl-alcoholic solution of the ketone ( $c = 0.392$ ) gave  $\alpha_D^{18} + 1.90^\circ$  in a 2-dcm. tube, and this value was unchanged after 1 day at the ordinary temperature. Three drops (0.05 c.c.) of ethyl-alcoholic potash (0.4487*N*) were then mixed with the solution and the fall in rotation was noted as below:

<i>t.</i>	$\theta.$	<i>t.</i>	$\theta.$	<i>t</i>	$\theta.$
1 min.	+1.87°	4 hours	+1.26°	24 hours	+0.31°
10 "	1.82	5 "	1.15	26 "	0.25
20 "	1.78	6 "	1.05	32 "	0.16
30 "	1.74	7 "	0.96	48 "	0.06
1 hour	1.63	8 "	0.88	54 "	0.05
2 hours	1.49	11 "	0.74	73 "	0.02
3 "	1.37	12 "	0.69		

*Action of Magnesium Benzyl Chloride on d-Benzyldeoxybenzoin.*  
 —The mixture of the ketone (0.6 g.) and the Grignard reagent prepared from benzyl chloride (2 g.) was boiled for 6 hours and then decomposed by ice and dilute sulphuric acid. The ethereal layer was dried, the ether expelled, and the oil triturated with hot light petroleum. The resulting solid was crystallised from light petroleum (b. p. 80–100°), *d*- $\alpha\beta$ -diphenyl- $\alpha\beta$ -dibenzylethyl alcohol,  $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\text{Ph}$ , separating in rosettes of needles, m. p. 167–168° (Found: C, 88.6; H, 7.0.  $\text{C}_{28}\text{H}_{26}\text{O}$  requires C, 88.8; H, 6.9%). In chloroform:  $l = 1$ ,  $c = 1.306$ ,  $\alpha_D^{20} + 2.02^\circ$ ,  $[\alpha]_D^{25} + 155^\circ$ .

We are indebted to Mr. Arthur Kelman Mills for the following observations.

*Action of Magnesium Benzyl Chloride on Ethyl  $\alpha$ -Alanine Hydrochloride.*—The ester hydrochloride (1 mol.) was heated for several hours with the Grignard reagent prepared from benzyl chloride (9 mols.). The mixture was decomposed by ice and ammonium chloride, the ether layer separated, the ether expelled, and the dibenzyl removed by steam distillation. The product was purified by crystallising first from light petroleum and then from rectified spirit.

*$\alpha$ -Amino- $\alpha\alpha$ -dibenzyl- $n$ -propyl alcohol,*



is moderately soluble in rectified spirit, from which it crystallises in plates, m. p. 93.5–94.5° (Found: C, 80.1; H, 8.4.  $\text{C}_{17}\text{H}_{21}\text{ON}$  requires C, 80.0; H, 8.3%).

*Action of Magnesium Benzyl Chloride on Ethyl  $\alpha$ -Phenylaminoacetate Hydrochloride.*—The ester hydrochloride (10 g., 1 mol.) was added to the Grignard reagent prepared from benzyl chloride (52.5 g., 9 mols.) and boiled for 3 hours. After decomposition with ice and ammonium chloride, the ethereal layer was separated and dried and from it an oil was obtained which was dissolved in hot light petroleum (b. p. 60–80°). 6.9 G. of solid crude amino-alcohol separated. This was recrystallised from rectified spirit; 6.0 g. of  $\beta$ -amino- $\alpha\alpha$ -dibenzyl- $\beta$ -phenylethyl alcohol, m. p. 125–126°, were then obtained. This compound has already been described by Thomas and Bettzieche (*Z. physiol. Chem.*, 1924, 140, 244), who used somewhat different experimental conditions from the above.



*Deamination of r-β-Amino-β-phenyl-α-dibenzylethyl Alcohol.*—To the solution of the amino-alcohol (4 g.) in 25% acetic acid (120 c.c.) an aqueous solution of sodium nitrite (3 g.) was added while the whole was maintained at 0°. The white solid which at first separated soon became viscous, and was extracted with ether. The product from the ethereal solution was dissolved in alcohol, and the solid which separated was crystallised twice from light petroleum (b. p. 40–60°). The resulting rosettes of needles consisted of benzyl αβ-diphenylethyl ketone,  $\text{CH}_2\text{Ph}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , m. p. 74–75°. For comparison, α-phenyl-ββ-dibenzylethylene glycol was prepared from ethyl *dl*-mandelate by the action of magnesium benzyl chloride, and dehydrated with concentrated sulphuric acid according to Orékhov (*Bull. Soc. chim.*, 1919, **25**, 111). When prepared in the latter manner, the ketone had m. p. 74–75° (Orékhov gives 75–76°), and there was no depression of the melting point when it was mixed with the product of the deamination.

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## CVII.—*Experiments on the Variation of the Angles of Crystals during Growth.*

By ERNEST SYDNEY HEDGES.

THE slight deviations from the theoretical angle which are to be observed in almost every crystal and the replacement of a theoretical face by a series of faces inclined to each other at minute angles are familiar to everyone who has carried out accurate measurements with a goniometer. In the practical measurement of these crystals it is customary to take the mean of such a set of readings, and in the majority of cases the method produces good results from a theoretical point of view. These vicinal faces are generally ignored, therefore, in determining the symmetry of the crystal. A study of the actual process of crystallisation, however, is incomplete if these forms are left neglected; in fact, regarded from a purely physical point of view, the existence of such faces may be a matter of some importance, and one which may help towards the elucidation of the process of crystallisation.

Several investigators have been interested in these variations and

have made exhaustive measurements on crystals which have been removed from the mother-liquor. Pfaff (*Sitzungsber. Physik. Med. Erlangen*, 1878, 10, 59), from a study of cubic crystals, concluded that the variations were exhibited by birefringent specimens, indicating a state of strain. Brauns (*Neues Jahrbuch*, 1887, 1, 136) could not confirm this opinion, and experiments with lead nitrate led him to suggest that the vicinal faces are really faces of low indices which have been distorted under the influence of gravity. Wulff (*Z. Kryst. Min.*, 1901, 34, 449) supposed the variations to be due to concentration currents playing over the crystal during its growth.

In order to study this problem more fully, a special type of goniometer was devised by Miers (*Phil. Trans.*, 1903, A, 202, 459), which permitted of the measurement of a crystal *during its growth*. The observations were concerned mainly with potassium alum and ammonium alum, and it was shown that the octahedral planes are invariably replaced by vicinal faces belonging to triakis octahedra which are subject to continual variations during the growth of the crystal.

The experiments described in the present paper are a continuation of this work, which the author has undertaken at the suggestion of Sir Henry Miers, using the same goniometer. The observations have been made over the course of the last three years and the work had to be discontinued abruptly. It is thought that the results so far achieved, although incomplete, may prove of interest and value.

#### EXPERIMENTAL.

*Orthorhombic System.*—For the purpose of studying the variations of angle exhibited by the vicinal faces during crystallisation, the crystal was immersed in a slightly supersaturated solution made up at a few degrees above room temperature and readings were taken at various time intervals for several hours. As a rule, immediately after immersion the images yielded by the vicinal faces became poor owing to a slight dissolution of the crystal. Crystallisation began quickly at first and subsequently became slower as the temperature of the solution approximated to that of the room. The substances used were sodium potassium tartrate and magnesium sulphate.

Two important results were derived from these experiments. (1) During the growth of a crystal the number of vicinal faces increases at first, generally reaching a maximum about one hour after immersion, after which the number of images steadily diminishes.

This process runs parallel with the rate of crystallisation, which increases to a maximum during the initial cooling and then slows

down as the crystallising temperature reaches that of the room. The following series of measurements, giving the readings for images from the vicinal faces occurring in a fixed portion of the prism zone of sodium potassium tartrate, illustrates this point. All columns of figures are to be read vertically.

TABLE I.

2.30 p.m.	2.45 p.m.	3.00 p.m.	3.15 p.m.	4.25 p.m.
269° 42½'	270° 10'	269° 55½'	270° 0'	272° 26½'
270 10	271 4½	270 5½	270 7½ (A)	271° 2'
272 35	271 14	271 8	270 15	272 31
	271 22	271 23½	270 57	272 40
	272 10	271 59	271 24	272 24
		272 27	272 0	272 47
		272 35	272 17	

This series of results is representative of the behaviour observed with nine crystals of sodium potassium tartrate. Similarly, Table II shows the total number of faces in the prism zone of magnesium sulphate yielding definite images at various times during the growth of a crystal, and is characteristic of the general results obtained with numerous other crystals.

TABLE II.

Time .....	1.25 p.m.	1.45 p.m.	2.10 p.m.	2.45 p.m.
No. of faces .....	9	13	16	11

(2) During the process of growth, the positions of the faces undergo rapid variations of considerable magnitude.

A rather extreme case was observed with the face marked A in Table I—an image chosen on account of its peculiar brightness. The image was kept under continuous observation for an hour and its position was read every minute. The readings vary in a very irregular fashion, the highest being 270° 10' and the lowest 269° 50'. The variation here is unusually large for an individual image, and this may correspond with the very rapid growth of the crystal which was observed in this particular experiment. The next series of readings, taken at five-minute intervals on a different crystal, is more characteristic of a general case: 205° 22', 205° 20', 205° 20½', 205° 19½', 205° 20', 205° 20½', 205° 20'.

An idea of the individual variations in the positions of the faces in the case of magnesium sulphate is gained from the following values for two bright images taken during growth. This example has been selected from series of readings taken with eleven different crystals of magnesium sulphate at various times.

4.40 p.m.	5.35 p.m.	6.15 p.m.
264° 7½'	264° 11½'	264° 14'
264 16	264 13½	264 16½

*Tetragonal System.*—A few experiments carried out with diammonium hydrogen phosphate confirmed the same general results. The faces on these crystals belong to two forms—prism and pyramid—and according to Groth no other forms have been observed. Both forms were found to be replaced by vicinal faces and the measurements of the prism zone given in Table III show that there is a maximum deviation of 20' from the right angle.

TABLE III.

2.40 p.m.			3.10 p.m.			3.35 p.m.		
118° 38'	298° 36'	}	118° 37½'	298° 41'	}	118° 36'	298° 34'	
	298 33			298 35				
208 37	28 34		208 35	28 34		208 33	28 34	
				28 20			28 20	

*Cubic System.*—More detailed experiments were conducted with sodium chlorate. Initially, the method was the same as in the foregoing case, i.e., the measurements were taken over the course of a few hours during the slow cooling of a solution. Under such conditions, the crystal is never in equilibrium with the mother-liquor. It is necessary to reproduce only one set of readings to represent the general results observed with nineteen crystals which have been examined.

Table IV records the complex images replacing the cube faces of a dextrorotatory sodium chlorate crystal. In addition to the exact position in the horizontal plane, the direction of those images which are out of the horizontal zone is indicated, although for the present purpose the distance above or below the zone was not measured.

TABLE IV.

1.45 p.m.		2.15 p.m.		2.45 p.m.		3.20 p.m.	
192° 27'		192° 27' Below.		192° 28' Below.		192° 28' Below.	
192 33		192 33½ Below.		192 45½		192 30	
192 48½		193 1½ Two vert., v.		192 59 On.		192 43 On.	
193 1½	} V. bright.			193 0 V. bright.		192 54	
193 3				193 2		192 59 Two vert.	
282 37		282 37½		282 37½		282 39	
282 46 Below.		282 40		282 40		282 48	
282 54		282 45 Below.		282 52½ Two vert.		282 51 V. bright	
282 58 Above.		282 51					
		282 54 V. bright.					
		282 56					
12 31		12 30		13 30		12 29	
12 37		12 36		13 0 Bright. Sl.		12 35	
12 57		12 56				12 58 Above, v.	
13 1	} V. bright.	13 0 Sl. above and v.		13 1½ above.		bright.	
13 3		13 2 bright.					
13 5							
102 40 Above.		102 36 Above.		102 43 Above.		102 43 Above.	
102 43 Three vert.		102 39 "		102 47 "		102 47 "	
102 46 Above.		102 43 "		102 52 On.		102 51 On.	
102 55 Two vert.		102 46 "		102 54 Below.		102 53 Below.	
		102 53 On.					
		102 57 Above.					

In this case, the mean of the vicinal faces *in the horizontal zone* replacing the cube face is calculated, and Table V, where these values are grouped, indicates that it is impossible to ascertain the true position of the cube faces by taking the mean of such readings.

TABLE V.

Mean Positions.						
Time.	A.	B.	C.	D.		
1.45 p.m.	192° 45½'	282° 45½'	12° 52'	102° 49'		
2.15 "	193 1½'	282 48	12 35	102 53		
2.45 "	193 0½'	282 57	12 46	102 52		
3.20 "	192 57	282 44½	12 32	102 51		
Suggested Cube Faces.						
1.45 "	193 1½'	282 54	13 1	102 55		
2.15 "	193 1½'	282 54	13 1	102 53		
2.45 "	193 0	282 52½	13 0	102 52		
3.20 "	192 59	282 51	12 58	102 51		

The table also gives the readings which would correspond to the cube faces on the assumption that the vicinal faces in accordance with the symmetry of the crystal belong to forms  $\{hko\}$  in a horizontal zone on one face and  $\{okl\}$  in a vertical zone on the adjacent face. The suggested cube face is the point of intersection of a vertical zone with a horizontal zone. The validity of the assumption is shown later. For example, at 2.15 p.m., the reading 193° 1½' represents an image in the horizontal plane which is duplicated in the vertical plane, and an examination of the tables shows that this face is prominent throughout the growth. Parallel to this face there occur the readings 13° 0' and 13° 2' arranged symmetrically about the suggested cube face, and inspection shows these faces to be prominent throughout. On the other hand, at right angles to these faces there is nothing to correspond. If the probable positions of the other pair of cube faces are worked out by the same method, they have a mean value of 282° 53' and 192° 53'.

*The Vicinal Faces in Relation to the Symmetry.*—The symmetry of sodium chlorate is the lowest type of the cubic system. There are no planes of symmetry, but there is a threefold axis passing through each solid angle of the cube and a two-fold axis normal to each cube face. If, therefore, the vicinal faces belong to the form  $\{hko\}$  and are consistent with the symmetry of the crystal, one would expect the vicinal faces replacing each pair of opposite cube planes to be disposed alike and to differ from the other pair in a perpendicular sense. This has been found to occur without exception in every crystal of sodium chlorate examined. In the cube faces A and C, the images are arranged mainly in the horizontal zone and in faces B and D they occur for the most part in a vertical zone.

Additional evidence on this point is observed when the crystal

is first immersed or during the incipient stages of dissolution when the temperature of the room rises. Under such conditions, a narrow band or haze of light appears in the field which represents either a rounded surface or a continuous series of facets etched on the crystal by the solvent. On one pair of parallel faces this band lies in the horizontal plane and on the other pair it is vertical. Conditions are often realised when such a vertical band is present simultaneously with well-developed images occurring either in the band or in the horizontal zone. This condition permits of a more certain way of determining the positions of the true cube faces, which is applicable even when the cube faces are themselves absent. Accurate measurements of sharp images appearing in the horizontal and vertical bands can be made and the point of intersection of the zones may be taken as the theoretical position of the cube face.

FIG. 1.

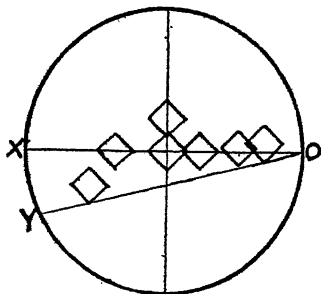
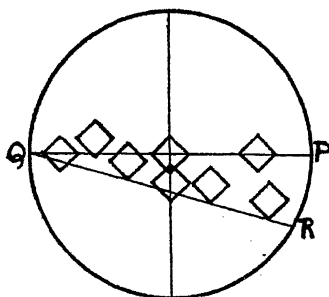


FIG. 2.



Thus, in one crystal, the positions of the vertical bands yielded by the faces B and D were measured as  $104^{\circ} 10'$  and  $284^{\circ} 10'$ , respectively. The true cube faces may be taken, therefore, as  $14^{\circ} 10'$ ,  $104^{\circ} 10'$ ,  $194^{\circ} 10'$ ,  $284^{\circ} 10'$ . The images actually yielded by the faces A and C were: A =  $13^{\circ} 54'$ ,  $14^{\circ} 4'$ ,  $14^{\circ} 20'$ ; C =  $194^{\circ} 0'$ ,  $194^{\circ} 20'$ . Although the cube faces are here not present, they are replaced by faces inclined symmetrically on either side.

The images, however, are not confined solely to the horizontal plane or to the vertical plane, and several occur which do not belong to either zone. Fig. 1 represents the appearance of the field in viewing the horizontally disposed face of a dextrorotatory crystal of sodium chlorate and may be compared with Fig. 2, which represents a similar state in a levorotatory crystal.

Attention may be directed to the upward trend from left to right in the faces A and C of the right-handed crystal and the downward trend from left to right in the corresponding faces of the left-handed crystal. Similarly, the trend of faces B and D was in the opposite direction in the two enantiomorphs. The angles XOY and PQR

were measured as  $16^\circ$  and  $17^\circ$ , respectively. This effect was noticed in two other specimens (right- and left-handed, respectively) which originated in the same batch of crystals. In later experiments, however, such a differentiation between the optical isomerides was not observed. No cases have appeared where the disposition is in an opposite sense to this, but those images which do not belong to either zone have been arranged in an apparently haphazard way.

Thus, although it is not possible to deduce the direction of optical rotation from the disposition of the vicinal faces, there is a tendency for these to be arranged in accordance with the optical properties of the crystal.

*Experiments on Slow Growth.*—With the object of studying the forms produced when the crystal is in true equilibrium with the solution, a crystal of sodium chlorate was induced to grow very slowly over a period of several weeks and readings were taken every morning about 9.30 a.m. before the room had warmed up. To realise favourable conditions for such experiments was a matter of considerable difficulty and in the damp Manchester atmosphere it was only found possible during the summer months; at other times of the year, the saturated solution tended to gain water often. When the necessary climatic conditions prevailed, the method adopted was to place a glass cover over the whole instrument during the night, when the crystal grew mainly by cooling, and to remove it during the day, when the crystal grew mainly by evaporation. In this way, crystallisation was always slow and a crystal did not increase in breadth by more than a quarter of an inch in a month.

The arrangement of the images during the first stages of slow growth was precisely similar to that already described, during the rapid growth of sodium chlorate crystals, the complex faces A and C differing in a perpendicular sense from the faces B and D. Again, the total number of images present underwent a progressive decrease with time. In addition to this, however, there was observed a most marked flattening of the forms during the process—that is to say, the images gradually approached one another until finally what appeared to be a single perfect cube face remained.

To take an example, a crystal was immersed on May 30th, 1924, and Table VI shows the horizontal extent of the complex face A (*i.e.*, the difference in minutes between the extreme images) on successive dates.

TABLE VI.

Date.	Extent.	Date.	Extent.	Date.	Extent.
May 30th	$43\frac{1}{2}'$	June 4th	$7\frac{1}{2}'$	June 18th	0
June 1st	37	„ 5th	9	„ 18th	0
„ 2nd	$8\frac{1}{2}$	„ 9th	14	„ 20th	0
„ 3rd	9	„ 12th	$2\frac{1}{2}$	„ 23rd	$19'$
				„ 30th	$8\frac{1}{2}$

The readings 0 for June 16th, 18th, and 20th indicate that on those days there was a single image in the field. An unusual spell of sunny weather over the week-end June 20th—23rd, during which the glass cover was left on, caused a partial dissolution of the crystal, so that the process takes a new start from that date.

Further, during slow growth, the forms flatten with time in both the horizontal and vertical zones, so that the four faces tend to become alike. The case was never realised where the crystal consists of four perfect cube faces existing simultaneously, although there seems to be no doubt that such a state may be arrived at under favourable conditions. Crystals have been observed where at different times each of the four faces in the zone has yielded an image corresponding to a true cube face. As a rule, only one pair of faces would give a single image in the theoretical place of the cube and the other pair would give duplicate images arranged symmetrically. For instance, a crystal after growing for a period of 24 days gave perfect single images at  $195^{\circ} 50'$  and  $15^{\circ} 50'$  and images of equal intensity arranged symmetrically at  $285^{\circ} 49'$ ,  $285^{\circ} 51'$ , and  $105^{\circ} 49'$ ,  $105^{\circ} 51'$ . The following morning, at  $195^{\circ} 50'$  and at  $15^{\circ} 50'$  there were duplicate images placed one minute above and below the zone, respectively. It is difficult to conceive of a more faithful representation of the symmetry of sodium chlorate.

*The Movement of the Faces.*—Evidence has been given of the continual variation in the positions of the images, and this point has received comment by Miers (*loc. cit.*), who stated that with potash alum the faces replaced each other *per saltum* in accordance with the law of rational indices. Throughout the present experiments, this has been the case with sodium chlorate and also with ammonium phosphate.

On the other hand, with magnesium sulphate, and particularly with sodium potassium tartrate, two kinds of movement have been observed : not only do the images move by successive replacement, but certain of the images were observed to travel across the field in a continuous manner. This motion was quite rapid, the path generally being about five to ten minutes of arc traversed in about one second of time. The most usual form in which the movement was manifested was when two bright faces occurred on the crystal close together; there was often a continuous migration of less bright but perfectly definite images from one to the other, the rate being of the order of one every few seconds. In some instances, an image was observed to leave a relatively fixed face, move out some distance, and then return. The latter fact seems to remove any doubt as to whether the movements may be a spurious effect due to the optical deflection of an image by currents of solution of



varying refractive index. Such deviations do undoubtedly occur, particularly if the solution is gently stirred, but are in the nature of a quick tremor of relatively small displacement during which the outline of the image becomes indefinite.

*Theoretical.*

As an explanation of vicinal faces Miers has suggested that the density of packing of molecules in a crystal is considerably greater than the density of packing in the saturated solution and that the molecules of solute, as they separate out of the crystallising solution, cannot squeeze themselves into the very close packing of a face with simple indices. On the other hand, the reticular density of a face inclined at an angle of a few minutes to one of the principal planes of the crystal is very low and much more suitable for the deposition of new units of the structure.

Some of the experiments which have been described above lend additional support to this view, for it is found that the crystal approximates more and more closely to the ideal form the slower the rate of growth. In fact, by carefully controlling the slow growth of sodium chlorate, single true cube faces may be obtained although these faces are generally absent in the ordinary way. Under such conditions of growth, it seems reasonable that the molecules of solute can easily take their places in a plane of high density.

*Summary.*

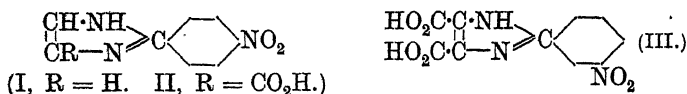
Measurements of the vicinal faces in crystals of sodium potassium tartrate, magnesium sulphate, diammonium hydrogen phosphate, and sodium chlorate, taken during the actual growth of the crystal, show that the number of faces undergoes an initial increase with time followed by a decline. The images undergo continual and rapid variations in position, generally by replacement, but in certain cases by continuous progression. The vicinal faces in sodium chlorate are consistent with the symmetry of the crystal, and a method is devised which enables the true positions of the ideal cube faces to be found even when they are absent. The slower the growth of the crystal, the more closely does it approximate to the ideal form. By carefully controlling the slow growth of sodium chlorate, single perfect cube faces may be developed. The experiments support the views of Miers on the cause of vicinal faces.

In conclusion, the author wishes to express his cordial thanks to Sir Henry A. Miers, F.R.S., for the constant encouragement and advice which he has received from him throughout the course of this work.

CVIII.—*The Nitration of Benzamidines.*

By ROBERT FORSYTH, VISHVANATH KRISHNA NIMKAR, and  
FRANK LEE PYMAN.

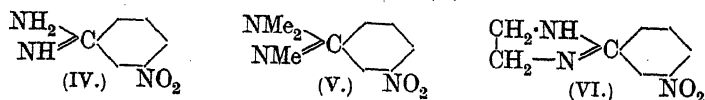
PYMAN and STANLEY (J., 1924, **125**, 2484) showed that nitration of 2-phenylglyoxaline and its 4(5)-monocarboxylic acid gave mainly the *p*-nitro-compounds (I and II), whereas 2-phenylglyoxaline-4 : 5-dicarboxylic acid gave mainly the *m*-nitro-compound (III).



In view of the fact that 2-phenylglyoxaline and its monocarboxylic acid yield salts with mineral acids whereas its dicarboxylic acid does not, they suggested that the different character of the doubly-linked nitrogen atom, that is, the nitrogen atom which takes part in salt formation (compare Burtles and Pyman, J., 1923, **123**, 361), was responsible for the different results. In 2-phenylglyoxaline, this nitrogen atom would be regarded as saturated or positive by combination with acid according as to whether the hypotheses of Flürscheim or Lapworth were employed, whilst in the dicarboxylic acid it would be regarded as unsaturated or negative.

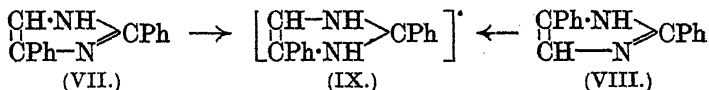
If this explanation were correct, then one would expect that nitration of benzamidine by the method employed for 2-phenylglyoxaline, that is, addition of the nitrate of the base to sulphuric acid, would yield mainly the *o*- and *p*-nitro-compounds, but as a matter of fact it proves to give more than 90% of *m*-nitrobenzamidine (IV).

Various possible explanations of the essentially different results of nitrating 2-phenylglyoxaline and benzamidine have now been examined. It might be suggested that since glyoxalines do not readily yield acyl derivatives, we should not postulate nitroamine formation in this case, but might reasonably do so in the case of benzamidines. An explanation would then be furnished analogous to that devised by Holmes and Ingold (J., 1925, **127**, 1800) to explain the difference between the results of nitrating secondary and tertiary benzylamines. Such an explanation, however, was found to be inapplicable in our case, since the nitration of benzenyltrimethylamidine, which cannot yield a nitroamine, gave more than 80% of *m*-nitrobenzenyltrimethylamidine (V).



Next, it might be thought that the different results of nitrating 2-phenylglyoxaline and benzamidine might be due to the fact that the two nitrogen atoms were linked together by a closed chain in the former compound and might neutralise each other's influence. This view was disproved by the nitration of 2-phenyl-4:5-dihydroglyoxaline, which gave more than 80% of 2-*m*-nitrophenyl-4:5-dihydroglyoxaline (VI).

It seems to us that the noteworthy difference between the results of nitrating 2-phenylglyoxaline and its dihydro-derivative are probably associated with the fact that glyoxalines have aromatic character whereas their dihydro-derivatives have not. It thus appears that the amidinium ion,  $\left[ \cdot \text{C} \begin{array}{c} \text{NHR} \\ \text{NR'R''} \end{array} \right]^+$ , which is contained in the salts of benzamidine, benzenyltrimethylamidinium, and 2-phenyl-4:5-dihydroglyoxaline, is strongly meta-directive, the nitrogen atoms exerting a similar influence to that of the oxygen atom in the carboxyl group. In the basic 2-phenylglyoxalines, the influence of the nitrogen atoms is suppressed, and the glyoxalinium ion produces an *op*-directive effect, due to the aromatic complex as a whole, and similar to that of phenyl in directing the *p*-nitration of diphenyl. The exceptional predominant *m*-nitration of the non-basic 2-phenylglyoxaline-4:5-dicarboxylic acid may be due possibly to the absence of salt formation in the case of this compound, and a difference in orienting properties between glyoxaline bases and glyoxalinium ions, for evidence of a difference in structure between glyoxalines and their salts may be found in the existence of the two isomeric bases 2:4- and 2:5-diphenylglyoxalines (VII and VIII), which yield a common ion (IX) (Burtles and Pyman, *loc. cit.*).



Nevertheless, the fact that the dicarboxylic acid yields 52% of the *m*- with 19% of the *p*-nitro-compound, whilst the monocarboxylic acid yields 52% of the *p*- with 19% of the *m*-compound, shows that the introduction of carboxyl groups into the glyoxaline nucleus of 2-phenylglyoxaline progressively diminishes the ratio of para- to meta-nitration of the benzene nucleus, and suggests, as an alternative explanation, for which we are indebted to Dr. King, that the results should be ascribed to the accumulation of acidic groups attached to the glyoxaline nucleus. In this sense, they are comparable with the results of nitrating benzyl chloride, benzylidene chloride, and benzotrichloride, where also the ratio of para- to meta-nitration is progressively diminished by the introduction of acidic groups

(Holleman, *Rec. trav. chim.*, 1914, **33**, 1). On the other hand, we found no support of this explanation, possibly owing to experimental difficulties, on the nitration of 4:5-dibromo-2-phenylglyoxaline (X),



which might be expected to yield a considerable proportion of the *m*-nitro-derivative, for here 4:5-dibromo-2-*p*-nitrophenylglyoxaline (XI) was isolated in a yield of 63% together with only 1.8% of an unidentified isomeride.

Nitration of 4(5)-bromo-2-phenylglyoxaline prepared by the reduction of the dibromo-compound with sodium sulphite proceeded less uniformly, possibly owing to nitration of the glyoxaline nucleus, but here the only product isolated was again the para-isomeride, 4(5)-bromo-2-*p*-nitrophenylglyoxaline. Another instance of the *p*-directive effect of the glyoxaline nucleus has been recorded by Tröger and Thomas (*J. pr. Chem.*, 1925, **110**, 42), who find that the nitration of lophine gives 2:4:5-tri-*p*-nitrophenylglyoxaline. Para-nitration of phenyl groups attached to the 2-position of glyoxalines having basic character thus seems to be the rule.

#### EXPERIMENTAL.

*Nitration of Benzamidine.*—Benzamidine nitrate,\* prepared from the base and dilute nitric acid, crystallised from alcohol in large, colourless, rhombic prisms, m. p. 128° (corr.) after softening from 124°, which are anhydrous and very easily soluble in water or hot alcohol (Found: C, 45.7, 45.6; H, 4.9, 5.0. C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>.HNO<sub>3</sub> requires C, 45.9; H, 4.9%). This salt (10 g.) was added gradually to concentrated sulphuric acid (20 c.c.) cooled in ice and salt. After  $\frac{1}{2}$  hour, the solution was heated for 2 hours at 100°, then diluted and mixed with aqueous solutions of barium hydroxide (50 g., hydrated) and barium chloride (46.7 g., hydrated). After removing barium sulphate, the aqueous solution was evaporated to dryness under diminished pressure, and the residue crystallised fractionally from alcohol, when 10.1 g. of pure *m*-nitrobenzamidine hydrochloride were isolated, that is, 91.7%.† The salts remaining in the mother-liquors were hydrolysed by boiling with 40 c.c. of 17% aqueous sodium hydroxide until ammonia was no longer evolved. On addition of concentrated hydrochloric acid, 0.62 g. of *m*-nitrobenzoic acid (m. p. 135°) separated, whilst ether collected a further 0.08 g. of less pure material (m. p. 118–120°). Mixtures of

\* This salt has not been described previously. The reference to it (*Jahresber.*, 1888, 1133) quoted by Beilstein is a mistake, and applies to the nitrite.

† All yields are expressed in percentage of the theoretical.

these products with pure *m*-nitrobenzoic acid melted at 137° and 126—131°, respectively. The amount of these crops represents 7·8% of the theoretical yield, making in all 99·5%, whence it is clear that the nitration of benzamidine yields almost wholly the meta-isomeride.

*m*-Nitrobenzamidine hydrochloride crystallises from alcohol in clusters of cream-coloured, prismatic needles, m. p. 251° (corr.) after sintering from 248°. It is anhydrous and readily soluble in water or hot alcohol (Found: C, 41·9; H, 4·0; Cl, 17·6. Calc., C, 41·7; H, 4·0; Cl, 17·6%). Tafel and Enoch (*Ber.*, 1890, 23, 1552), who prepared this salt by the interaction of the hydrochloride of *m*-nitrobenziminioethyl ether with ammonia, give m. p. 240°. The identity and purity of our preparation were established by hydrolysing the salt (1 g.) with 8·5% aqueous sodium hydroxide (40 c.c.), and adding concentrated hydrochloric acid, when 0·564 g. of *m*-nitrobenzoic acid, m. p. 140° (corr.), separated, and 0·25 g., m. p. 139°, was collected by ether, the total yield being 98·2%. The identity of these crops with *m*-nitrobenzoic acid was established by the mixed-melting point method. The first crop was also analysed (Found: C, 50·3; H, 3·0. Calc., C, 50·3; H, 3·0%).

*Nitration of Benzenyltrimethylamidine.*—*Benzenyltrimethylamidine nitrate* was prepared by the double decomposition of aqueous solutions of silver nitrate and the corresponding hydriodide, previously called dimethylamidobenzenylmethylimidine hydriodide (Pyman, J., 1923, 123, 3372). It crystallises from alcohol in large, colourless, prismatic rods, m. p. 195—196° (corr.). It is anhydrous and readily soluble in water or hot alcohol (Found: C, 53·2; H, 6·5; N, 18·5.  $C_{10}H_{14}N_2 \cdot HNO_3$  requires C, 53·3; H, 6·7; N, 18·7%). This salt (10 g.) was added gradually to concentrated sulphuric acid cooled in ice and salt. The solution was kept for 1 hour at the room temperature, heated for 2 hours at 100°, diluted with water, and mixed with aqueous solutions of barium hydroxide (50 g., hydrated) and barium chloride (46·7 g., hydrated). After removing barium sulphate, the aqueous solution was evaporated to dryness under diminished pressure, when a pale yellow syrup was obtained. Since the hydrochlorides showed little tendency to crystallise, the syrup was diluted and mixed with excess of aqueous sodium iodide, when the hydriodides separated as an oil which soon solidified. ~~After~~ numerous crystallisations from alcohol, using sulphur dioxide as a decolorising agent, 11·01 g. of pure *m*-nitrobenzenyltrimethylamidine hydriodide were isolated (yield 73·9%). The substance remaining in the mother-liquors was hydrolysed with aqueous sodium hydroxide; strong hydrochloric acid then precipitated 0·69 g. of *m*-nitrobenzoic acid, m. p. 133—137°. The filtrate was unfortunately lost.

On recrystallising the acid, 0.52 g. was obtained pure (m. p. 140°) and a further 0.164 g., m. p. 138°. They were identified as *m*-nitrobenzoic acid by the mixed-melting point method. The amount of these crops represents 9.3% of the theoretical yield, making in all 83.2%.

*m*-Nitrobenzenyltrimethylamidine hydriodide crystallises from alcohol in pale lemon-yellow needles, m. p. 243—246° (corr.; decomp.). It is anhydrous, and sparingly soluble in water or cold alcohol, but readily soluble in acetone (Found: C, 35.8; H, 4.1; I, 37.9.  $C_{10}H_{13}O_2N_3.HI$  requires C, 35.8; H, 4.2; I, 37.9%).

The identity and purity of this salt were established by hydrolysing 1.675 g. with aqueous sodium hydroxide, and acidifying the solution, when 0.67 g. of *m*-nitrobenzoic acid, m. p. 140°, was precipitated, and 0.16 g., m. p. 130°, collected from the filtrate by means of ether, the total yield being 99%. Both crops were identified as *m*-nitrobenzoic acid by the mixed-melting point method, and the first crop was also analysed (Found: C, 50.5; H, 3.0. Calc., C, 50.3; H, 3.0%).

*2-Phenyl-4:5-dihydroglyoxaline*.—Hofmann (*Ber.*, 1888, 21, 2334) states, without giving any details, that this base is best prepared by heating dibenzoylthylenediamine in a stream of hydrogen chloride, and this method was adopted after it had been found that dibenzoylthylenediamine was completely hydrolysed by boiling with concentrated sulphuric acid (3 c.c. per g.) for 10 minutes, and was only slowly attacked by boiling concentrated hydrochloric acid (10 c.c. per g.) when, after 2 hours, 82% was recovered unchanged. Ten grams of dibenzoylthylenediamine (prepared from ethylenediamine monohydrate by the Schotten-Baumann method in 91% yield) were heated to 250°, and dry hydrogen chloride was passed through the molten substance for 1 hour. The product was dissolved in hot water; on keeping, benzoic acid and 0.3 g. of unchanged material separated. The filtrate was basified and extracted with ether, which gave 4.56 g. of 2-phenyl-4:5-dihydroglyoxaline, m. p. 100° (yield 83.7%). It crystallised from acetone in colourless, prismatic needles, m. p. 102—103° (corr.). Hofmann gives m. p. 101°.

The nitrate crystallises from acetone in large, colourless, rhombic prisms, which are hydrated to a variable extent. After drying at 98°, it is anhydrous and melts at 118—119° (corr.) after softening from 117°. On cooling, it resolidifies and then melts sharply at 123° (corr.), but on recrystallising this modification, it reverts to the original form, m. p. 118—119°. This salt was described previously by Forssell (*Ber.*, 1892, 25, 2135), who does not record its m. p.

*Nitration of 2-Phenyl-4:5-dihydroglyoxaline*.—The anhydrous

nitrate (10.55 g.) was added to concentrated sulphuric acid (21 c.c.) cooled in ice and salt. The solution was kept for 1 hour at room temperature and then heated for 2 hours at  $100^{\circ}$ . The product was treated with barium hydroxide and barium chloride, just as the nitration product of benzamidine, to give the hydrochloride, which was crystallised from alcohol, when 10.47 g. of pure 2-*m*-nitrophenyl-4 : 5-dihydroglyoxaline hydrochloride were obtained, that is, 84.4%. The mother-liquors contained hydrochlorides (m. p.  $195-200^{\circ}$ ) which could not be separated either as such or as hydriodide or picrate, and the material was therefore oxidised with alkaline permanganate, when a mixture of nitrobenzoic acids was obtained, from which pure *m*-nitrobenzoic acid was isolated in a yield of 3%.

2-*m*-Nitrophenyl-4 : 5-dihydroglyoxaline hydrochloride crystallises from alcohol in coarse, yellow needles containing  $1\text{H}_2\text{O}$ , which is lost at  $100^{\circ}$ . After drying, it has m. p.  $249-251^{\circ}$  (corr.). It is readily soluble in water or hot alcohol, but sparingly soluble in acetone (Found in air-dried salt : loss in a vacuum over  $\text{H}_2\text{SO}_4$ , 7.4, 7.3.  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 7.3%. Found in dried salt : C, 47.6; H, 4.3; Cl, 15.6.  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3\cdot\text{HCl}$  requires C, 47.5; H, 4.4; Cl, 15.6%). The hydriodide crystallises from water in pale yellow, prismatic needles, m. p.  $207-209^{\circ}$  (corr.), which are anhydrous and sparingly soluble in water (Found : I, 40.0.  $\text{C}_9\text{H}_9\text{O}_2\text{N}_3\cdot\text{HI}$  requires I, 39.8%).

The picrate crystallises from water or alcohol in fine, lemon-yellow needles, m. p.  $224-225^{\circ}$  (corr.). It is anhydrous and sparingly soluble in hot water or hot alcohol, but very readily soluble in acetone.

The orientation of the nitro-group in 2-*m*-nitrophenyl-4 : 5-dihydroglyoxaline was established by oxidation. The hydrated hydrochloride (1.23 g.) in hot water (50 c.c.) was boiled with 17% aqueous sodium hydroxide (20 c.c.) and sufficient aqueous potassium permanganate to give a permanently pink solution. After adding alcohol and filtering, the solution was concentrated and acidified with hydrochloric acid, when 0.577 g. of *m*-nitrobenzoic acid, m. p.  $140^{\circ}$  (corr.), was deposited, whilst ether extracted a further 0.048 g., m. p.  $125-128^{\circ}$ , from the mother-liquor. Mixtures of the two crops with pure *m*-nitrobenzoic acid had m. p.  $140^{\circ}$  (corr.) and  $132-135^{\circ}$ , respectively. The total yield is 74.9%.

*Bromination of 2-Phenylglyoxaline.*—A solution of 1.75 c.c. of bromine (1 mol.) in chloroform (15 c.c.) was added gradually to 2-phenylglyoxaline (5 g.) in chloroform (40 c.c.). After keeping for 15 minutes, the colourless precipitate of 4 : 5-dibromo-2-phenylglyoxaline hydrobromide, m. p.  $250-255^{\circ}$ , was collected, and this

gave on repeated treatment with cold water the base (4.3 g.), m. p. 137—138°. The chloroform mother-liquors were distilled with steam to remove solvent and excess of bromine, and the aqueous residue deposited 0.5 g. of the crude dibromo-base, m. p. 136—138°. The total yield is thus 46%. The final mother-liquors were basified with sodium carbonate and gave crude 2-phenylglyoxaline (2.5 g.; m. p. 138—140°).

4 : 5-Dibromo-2-phenylglyoxaline crystallises from acetone in colourless cubes, which decompose at about 141° (corr.) after darkening earlier (Found : C, 36.0; H, 2.0; Br, 52.8.  $C_9H_6N_2Br_2$  requires C, 35.8; H, 2.0; Br, 53.9%). It is insoluble in cold water and resinifies when heated with water. It is soluble in warm dilute mineral acids, aqueous sodium hydroxide, or ammonia. It is readily soluble in alcohol or acetone, and fairly readily soluble in ether or chloroform.

The hydrochloride crystallises from dilute hydrochloric acid in colourless needles, m. p. 235—237° (corr.). It yields the base on treatment with water. The picrate forms yellow plates, from alcohol, m. p. 170—172° (corr.).

*Nitration.* Potassium nitrate (3.3 g.; 1 mol.) was added to a cold solution of 4 : 5-dibromo-2-phenylglyoxaline (10 g.) in concentrated sulphuric acid (40 c.c.). After heating for 2 hours at 100°, the solution was poured into water, when 4 : 5-dibromo-2-*p*-nitrophenylglyoxaline was precipitated; the filtrate was basified with sodium carbonate, when an isomeric base separated. After crystallising these products from alcohol, 7.0 g. of the *p*-nitro-compound (yield 63%) and 0.2 g. of the isomeride (yield 1.8%) were obtained in a pure state.

4 : 5-Dibromo-2-*p*-nitrophenylglyoxaline crystallises from alcohol in orange needles, m. p. 220—222° (corr.) (Found in air-dried base : loss in a vacuum over  $H_2SO_4$ , 9.3, 9.3.  $C_9H_5O_2N_3Br_2 \cdot 2H_2O$  requires  $2H_2O$ , 9.4%. Found in dried base : C, 31.2; H, 1.8; N, 12.1; Br, 45.8.  $C_9H_5O_2N_3Br_2$  requires C, 31.1; H, 1.4; N, 12.1; Br, 46.1%). It is insoluble in cold water, and resinifies on heating with water. It is insoluble in cold dilute mineral acids, but dissolves slightly on warming. It dissolves in aqueous sodium hydroxide, ammonia, and sodium carbonate, giving red, orange, and yellow solutions, respectively. It is readily soluble in alcohol, acetone, or ether. On oxidation with alkaline permanganate, it gave *p*-nitrobenzoic acid, which was identified by the mixed-melting point method. 4 : 5-Dibromo-2-*o*(or *m*)-nitrophenylglyoxaline crystallises from dilute alcohol in lemon-yellow, glistening plates, m. p. 181—182° (corr.), which are anhydrous (Found : C, 31.0; H, 2.0; N, 12.1.  $C_9H_5O_2N_3Br_2$  requires C, 31.1; H, 1.4; N, 12.1%). It is insoluble



in hot or cold water, slightly soluble in dilute mineral acids, and readily soluble in aqueous sodium hydroxide, ammonia, or sodium carbonate, giving red, orange, and yellow solutions. The quantity available did not permit the identification of the acid produced on oxidation.

*Reduction of 4:5-Dibromo-2-phenylglyoxaline.*—Hot solutions of 4:5-dibromo-2-phenylglyoxaline (5 g.) in alcohol (125 c.c.) and hydrated sodium sulphite (20.5 g.) in water (200 c.c.) were mixed and boiled for 8 hours under reflux. After the alcohol had been removed, a crystalline precipitate (m. p. 185—187°) was deposited, which was separated, by fractional precipitation by hydrochloric acid from its solution in aqueous sodium hydroxide, into 4(5)-bromo-2-phenylglyoxaline (1.43 g.; m. p. 205—206°; yield 39%) and unchanged dibromo-base (1.36 g.).

4(5)-Bromo-2-phenylglyoxaline crystallises from dilute alcohol in small, white needles, m. p. 206—207° (corr.) (Found: C, 48.3; H, 3.1; N, 12.2; Br, 35.7.  $C_9H_7N_2Br$  requires C, 48.4; H, 3.1; N, 12.6; Br, 35.9%). It is slightly soluble in hot water, readily soluble in alcohol or acetone, and moderately readily soluble in ether. It is soluble in warm dilute acids, aqueous sodium hydroxide, or ammonia, but insoluble in aqueous sodium carbonate.

The *hydrochloride* crystallises from dilute hydrochloric acid in hard, white needles, which lose  $1H_2O$  in a vacuum over sulphuric acid and then melt at 118—119° (corr.) (Found in air-dried salt: loss in a vacuum over  $H_2SO_4$ , 6.6.  $C_9H_7N_2Br \cdot HCl \cdot H_2O$  requires  $H_2O$ , 6.5%. Found in dried salt: Cl, 13.8.  $C_9H_7N_2Br \cdot HCl$  requires Cl, 13.7%). On heating at 100°, the vacuum-dried salt suffers a further loss owing to dissociation. The *picrate* crystallises from alcohol in yellow plates, m. p. (air-dried) 164—165° (corr.).

*Nitration.* Potassium nitrate (0.76 g.; 1 mol.) was added to a cold solution of 4(5)-bromo-2-phenylglyoxaline (2 g.) in concentrated sulphuric acid (4 c.c.). After heating for 2 hours at 100°, the solution was poured into water, filtered from a yellow precipitate (1.0 g.; m. p. 95—110°), which was not worked up, and basified with sodium carbonate, when a further precipitate (1.7 g.; m. p. 180—182°) was collected. After crystallisation from dilute alcohol, this gave pure 4(5)-bromo-2-*p*-nitrophenylglyoxaline (0.75 g.; yield 31%).

4(5)-Bromo-2-*p*-nitrophenylglyoxaline crystallises from glacial acetic acid in yellow needles, m. p. 222—223° (corr.) (Found: loss at 100°, 18.1.  $C_9H_6O_2N_3Br \cdot CH_3 \cdot CO_2H$  requires loss of  $CH_3 \cdot CO_2H$ , 18.3%. Found in substance dried at 100°: C, 40.0; H, 2.5; N, 15.8.  $C_9H_6O_2N_3Br$  requires C, 40.3; H, 2.2; N, 15.7%).

It is insoluble in hot water, readily soluble in alcohol, ether, acetone, or glacial acetic acid, and moderately readily soluble in

chloroform. It is soluble in aqueous mineral acids, and dissolves in aqueous alkalis, including sodium carbonate, giving yellow to red solutions.

On oxidation with alkaline permanganate, it gave *p*-nitrobenzoic acid, which was identified by the mixed-melting point method.

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### CIX.—*Derivatives of Tetrahydrocarbazole. Part V.* *Carboxylic Acids.*

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THE tetrahydrocarbazolecarboxylic acids hitherto described have the carboxyl group either in the reduced portion of the carbazole molecule (Perkin, J., 1904, 85, 418; Baeyer and Tutein, *Ber.*, 1889, 22, 2184) or attached to the nitrogen atom (Perkin and Plant, J., 1923, 123, 683). We have now prepared the four isomeric acids in which the carboxyl group is attached to the benzene nucleus (for the scheme of numbering the positions in tetrahydrocarbazole, see J., 1923, 123, 677) by Fischer's method for the synthesis of indole derivatives. In this way, the hydrazones made by condensing cyclohexanone with *o*- and *p*-hydrazinobenzoic acid lost ammonia and gave respectively tetrahydrocarbazole-8- and 6-carboxylic acids, whilst the hydrazone from *m*-hydrazinobenzoic acid by the same process gave a mixture of two acids, one of which must have the carboxyl group in the 5- and the other in the 7-position. This experience is contrary to that which was found in the case of cyclohexanone-*m*-nitrophenylhydrazone, from which only one of the two possible isomeric nitrotetrahydrocarbazoles, assumed to be 7-nitrotetrahydrocarbazole, was obtained on closing the indole ring (Borsche, Witte, and Bothe, *Annalen*, 1908, 359, 68; Perkin and Plant, J., 1921, 119, 1828). Baeyer and Tutein (*loc. cit.*) prepared an acid which may be tetrahydrocarbazole-2 or 4-carboxylic acid from the phenylhydrazone of cyclohexanone-3-carboxylic acid.

The constitutions of these four tetrahydrocarbazolecarboxylic acids are confirmed by the fact that they easily give tetrahydrocarbazole on distillation with soda-lime.

#### EXPERIMENTAL.

*Tetrahydrocarbazole-6-carboxylic Acid.*—The crude hydrochloride of *p*-hydrazinobenzoic acid, prepared from *p*-aminobenzoic acid (25 g.) by the method of Fischer (*Annalen*, 1882, 212, 337), was

dissolved in hot water (350 c.c.), treated with an excess of sodium acetate, and then with *cyclohexanone* (18 c.c.); on shaking, *cyclohexanone-p-carboxyphenylhydrazone* separated. It crystallised from glacial acetic acid in yellow prisms, m. p.  $236^{\circ}$  (decomp.) (Found : N, 12.5.  $C_{13}H_{16}O_2N_2$  requires N, 12.1%).

The crude hydrazone was added to water (200 c.c.) and sulphuric acid (40 c.c.) and the mixture warmed to boiling. The *tetrahydrocarbazole-6-carboxylic acid* that separated crystallised from dilute alcohol in colourless plates, m. p.  $282^{\circ}$  (Found : N, 6.6.  $C_{13}H_{13}O_2N$  requires N, 6.5%).

The *methyl* ester was produced by boiling the acid with methyl alcohol containing a little sulphuric acid for 4 hours, and precipitating by the addition of dilute aqueous ammonia. It crystallised from dilute acetic acid in colourless leaves, m. p.  $158^{\circ}$  (Found : N, 5.9.  $C_{14}H_{15}O_2N$  requires N, 6.1%). The *ethyl* ester was prepared in a similar way and separated from dilute alcohol in small, colourless prisms, m. p.  $119^{\circ}$ .

*Tetrahydrocarbazole-8-carboxylic Acid*.—The hydrochloride of *o*-hydrazinobenzoic acid was converted by a process similar to that described above into *cyclohexanone-o-carboxyphenylhydrazone*, which separated from benzene in pale yellow needles, m. p.  $162^{\circ}$  (Found : N, 12.0.  $C_{13}H_{16}O_2N_2$  requires N, 12.1%). On warming the hydrazone (6 g.) with water (120 c.c.) and sulphuric acid (30 c.c.), *tetrahydrocarbazole-8-carboxylic acid* separated and, on recrystallisation from benzene, it was obtained in colourless prisms, m. p.  $203^{\circ}$  (Found : N, 6.5.  $C_{13}H_{13}O_2N$  requires N, 6.5%).

The *methyl* ester crystallises from methyl alcohol in long, colourless prisms, m. p.  $124^{\circ}$  (Found : N, 5.9.  $C_{14}H_{15}O_2N$  requires N, 6.1%). The *ethyl* ester separates from dilute alcohol in colourless needles, m. p.  $76^{\circ}$  (Found : N, 5.8.  $C_{15}H_{17}O_2N$  requires N, 5.7%).

*Tetrahydrocarbazole-5- and 7-carboxylic Acids*.—*cyclohexanone-m-carboxyphenylhydrazone*, prepared from *m*-hydrazinobenzoic acid in the usual way, crystallised from dilute alcohol in orange prisms, m. p.  $176^{\circ}$  (decomp.) (Found : N, 11.9.  $C_{13}H_{16}O_2N_2$  requires N, 12.1%). The crude hydrazone was converted into a mixture of *tetrahydrocarbazole-5- and 7-carboxylic acids* on warming with dilute sulphuric acid. The two acids were isolated from the product by fractional crystallisation from either glacial acetic acid or aqueous acetone, and purified by conversion into their methyl esters, from which they were readily obtained on saponification. The acid which separated first in both cases was finally recrystallised from glacial acetic acid and obtained in colourless prisms, m. p.  $287^{\circ}$  (Found : N, 6.6.  $C_{13}H_{13}O_2N$  requires N, 6.5%). Its *methyl* ester crystallised from methyl alcohol in colourless needles, m. p.

155°, and its *ethyl* ester from dilute alcohol in small, colourless plates, m. p. 146°.

The isomeric *tetrahydrocarbazolecarboxylic acid* was ultimately obtained from glacial acetic acid in almost colourless prisms, m. p. 210° (Found : N, 6.1.  $C_{13}H_{13}O_2N$  requires N, 6.5%). Its *methyl* ester separated from aqueous alcohol in colourless prisms, m. p. 93° (Found : N, 6.1.  $C_{14}H_{15}O_2N$  requires N, 6.1%).

The higher-melting acid (m. p. 287°) is the main constituent of the product of this reaction and from 30 g. of the crude material 16 g. of this acid and 6 g. of the isomeride (m. p. 210°) were isolated in a pure condition.

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### CX.—*The Oximes of 2:4-Dinitrobenzil and the Beckmann Change.*

By GERALD BISHOP and OSCAR L. BRADY.

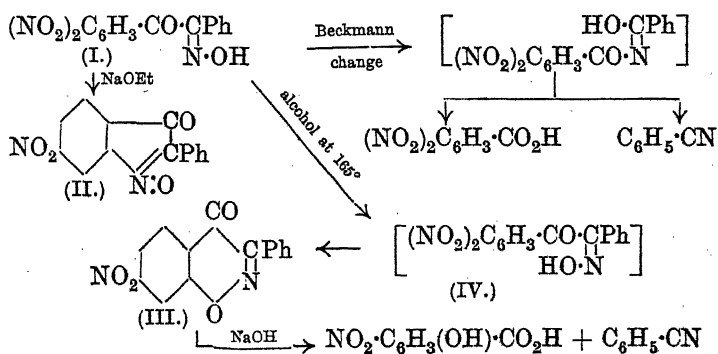
In a previous communication (J., 1922, **121**, 2364), two substances, regarded as monoximes of 2:4-dinitrobenzil, were described to which, on account of their behaviour in the Beckmann change, the following structures were assigned :



Further investigation, however, has shown that the supposed  $\beta$ -oxime was a mixture and that its reactions were untrustworthy guides to its constitution. Consequently, our early view of the configurations of the substances requires modification. We are now of opinion that their reactions are best explained by adopting Meisenheimer's view that the Beckmann change takes place in a *trans*- and not in a *cis*-sense (*Ber.*, 1921, **54**, 3206; 1924, **57**, 276, 282, 289), ring closure being assumed to involve no change in configuration (compare, however, Kuhn and Ebel, *Ber.*, 1925, **58**, 919; Böseken, *ibid.*, p. 1470; Meisenheimer, *ibid.*, p. 1491). The  $\alpha$ -oxime has accordingly been given the configuration (I). The Beckmann change leads to benzonitrile and 2:4-dinitrobenzoic acid as previously described. By boiling with the calculated quantity of sodium dissolved in alcohol, the  $\alpha$ -oxime is converted, by elimination of nitrous acid, into a brilliant scarlet compound which, on account of its colour, we consider to be 6-nitro-3-keto-

2-phenyl- $\psi$ -indole-1-oxide (II), the  $\alpha$ -oxime, since the oxygen atom is remote from the nitro-group, reacting in the nitron form. This compound on treatment with excess of alkali gives benzaldehyde and an amorphous compound, thus behaving similarly to the  $\alpha$ -oxime itself when treated with excess of aqueous sodium hydroxide. When the  $\alpha$ -oxime is heated in alcohol to 165°, nitrous acid is eliminated and 7-nitro-4-keto-3-phenyl-1:2-benzoxazine (III) is formed. That this compound is not produced by the action of alkali on the  $\alpha$ -oxime suggests that at the high temperature the oxime undergoes an isomeric change analogous to that of the oximes of benzil under similar conditions; in the new oxime (IV) thus produced, the hydroxyl and nitro-groups are vicinal and consequently nitrous acid is readily eliminated. 7-Nitro-4-keto-3-phenyl-1:2-benzoxazine on hydrolysis gives benzonitrile and 4-nitrosalicylic acid. The benzoxazine melts, by an unfortunate coincidence, at the same temperature (169°) as 4-nitrosalicylonitrile, and we have found that the compound produced by the action of alkali on the supposed  $\beta$ -oxime and described in our previous paper as 4-nitrosalicylonitrile (*loc. cit.*, p. 2369), and for the identification of which we relied on the melting point and hydrolysis to 4-nitrosalicylic acid, was in fact this benzoxazine.

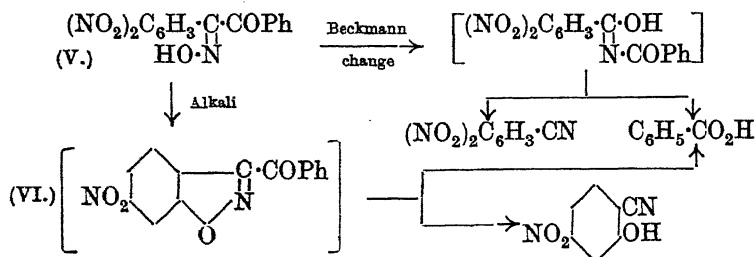
The reactions of the  $\alpha$ -oxime may be summarised thus :



The action of excess of free hydroxylamine on 2:4-dinitrobenzil, by which the supposed  $\beta$ -oxime was obtained, yields a complex mixture, from which 7-nitro-4-keto-3-phenyl-1:2-benzoxazine (III), the  $\alpha$ -oxime (I), and the pure  $\beta$ -oxime (V) have been isolated. The formation of the benzoxazine suggests that the unknown oxime (IV) is first produced and loses nitrous acid with great ease in the presence of excess of hydroxylamine.

The  $\beta$ -oxime, in the Beckmann change, gives benzoic acid and 2:4-dinitrobenzonitrile. On heating with alkali, it gives benzoic

acid and 4-nitrosalicylonitrile through the unstable isooxazole (VI). Its reactions may be represented thus :



There was also evidence that the crude oximation mixture contained the fourth oxime,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{-C}\cdot\text{COPh}$ . The presence of

this would account for the isolation, in the previously described experiments, of 2 : 4-dinitroaniline after the supposed  $\beta$ -oxime had undergone the Beckmann change. In a subsequent similar experiment with the crude oximation mixture, we were unable to separate the dinitroaniline from the other products, but isolated 2 : 4-dinitrophenol by heating with concentrated alkali, acidifying, and distilling in steam.

## EXPERIMENTAL.

$\alpha$ -2:4-Dinitrobenzilmonoxime.—The preparation is described in our previous paper. The  $\alpha$ -monoxime (3 g.) was heated for 5 hours with absolute alcohol (5 c.c.) in a sealed tube at 165°. On cooling, a colourless, crystalline compound separated which after crystallisation from alcohol gave 7-nitro-4-keto-3-phenyl-1:2-benzoxazine (III), m. p. 169° (Found: N, 10.4.  $C_{14}H_8O_4N_2$  requires N, 10.4%). This compound was identical in properties with the supposed 4-nitrosalicylonitrile previously obtained by the action of alkali on the impure  $\beta$ -oxime (Bishop and Brady, *loc. cit.*) and on admixture did not depress its melting point. 7-Nitro-4-keto-3-phenyl-1:2-benzoxazine was boiled for a short time with 10% sodium hydroxide; the odour of benzonitrile was observed and on distilling in steam this nitrile was obtained in the distillate; the residue, on being acidified, gave a precipitate from which 4-nitrosalicylic acid was obtained by crystallisation.

The action of alkali in excess on the  $\alpha$ -oxime was described in the previous paper. When, however, the oxime (5 g.), dissolved in absolute alcohol (20 c.c.) containing the calculated quantity of sodium to give the sodium salt (0.36 g.), was boiled for 15 minutes, a brilliant scarlet precipitate of 6-nitro-3-keto-2-phenyl- $\psi$ -indole 1-oxide formed which crystallised from alcohol as a red, crystalline

powder, m. p.  $198^{\circ}$  (Found: C, 62.5; H, 3.1; N, 10.5.  $C_{14}H_8O_4N_2$  requires C, 62.7; H, 3.0; N, 10.4%). Nitrite was detected in the mother-liquor from the preparation. Boiled with excess of aqueous alkali, the compound behaves in a similar manner to the  $\alpha$ -oxime, giving benzaldehyde and an amorphous product.

$\beta$ -2 : 4-Dinitrobenzilmonoxime.—A solution of 2 : 4-dinitrobenzil in alcohol cooled in ice was treated with an alcoholic solution of 3 equivalents of hydroxylamine. After a few moments, crystals of 7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine began to separate and after 12 hours these were collected and the filtrate from them was diluted with water ( $\frac{1}{4}$  vol.); a small quantity of impure  $\alpha$ -monoxime was then precipitated. The filtrate from the  $\alpha$ -oxime was poured into excess of water, kept over-night, and the precipitate repeatedly crystallised from dilute alcohol until its melting point was constant;  $\beta$ -2 : 4-dinitrobenzilmonoxime, m. p.  $168^{\circ}$ , was thus obtained (Found: N, 13.4. Calc., N, 13.3%).

A solution of the  $\beta$ -oxime in ether was cooled in ice, and the calculated quantity of phosphorus pentachloride added. After 12 hours, ice-water was added, and the mixture then kept for 3 hours. The ether layer was shaken several times with 2*N*-sodium carbonate and evaporated; 2 : 4-dinitrobenzonitrile, identified by comparison with an authentic specimen, was thus obtained. The alkaline extracts on acidification and re-extraction with ether gave benzoic acid.

The  $\beta$ -oxime was boiled under reflux for an hour with 2*N*-sodium hydroxide; no darkening or evolution of ammonia occurred as with the  $\alpha$ -oxime, and on cooling and saturating with carbon dioxide 4-nitrosalicylonitrile crystallised. This was identified by comparison with a specimen prepared from 2 : 4-dinitrobenzaldoxime (Borsche and Oppenheimer, *Annalen*, 1912, 390, 10). The carbonate solution, after removal of dissolved nitrosalicylonitrile with ether, gave benzoic acid on being acidified and extracted with ether.

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UNIVERSITY COLLEGE, LONDON. [Received, January 25th, 1926.]

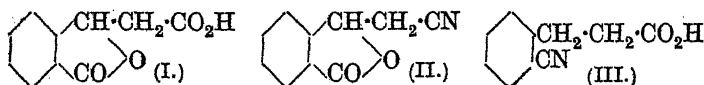
## CXI.—*Synthetical Work on the isoQuinoline Alkaloids.* *Part II. A Method of Opening the Rings of Cyclic Ketones.*

By GEORGE ALFRED EDWARDS.

THE reactions herein described were investigated with the object of obtaining derivatives of  $\beta$ -o-cyanophenylpropionic acid and of o-carboxyphenylacetonitrile, such substances being required for attempts to synthesise ten-membered rings of the cryptopine type.

The sodium salt of 1-nitroso- $\beta$ -naphthol when heated to  $180^\circ$  with sand gives sodium *o*-cyanocinnamate in poor yield (D.R.-P. 116223). This reaction was examined in the hope of bringing about the same change by less violent means. 1-Nitroso- $\beta$ -naphthol was converted by benzoyl chloride and cold caustic soda solution into a benzoyl derivative, which slowly hydrolysed in warm caustic soda solution, yielding benzoic acid and the *o*-cyanocinnamic acid of m. p.  $137^\circ$  (D.R.-P. 411955). The separation of the benzoic acid was rather troublesome, so it is fortunate that benzoyl chloride can be replaced by either benzene- or toluene-sulphonyl chloride, the acyl derivative produced being in each case easily hydrolysed to the above cyano-acid.

This 2-cyanocinnamic acid was at first thought to be *o*-carboxycinnamonitrile, since on hydrolysis it gave *o*-carboxycinnamic acid, and since, if its formation followed the normal course of the Beckmann reaction, ring opening might take place in two ways, thus:  $R \cdot C(NO_2) \cdot COR' \rightarrow R \cdot CO \cdot NH \cdot COR' \rightarrow$  either  $R \cdot CO_2H$  and  $R'CN$  or  $RCN$  and  $R' \cdot CO_2H$ . *o*-Carboxycinnamonitrile was therefore synthesised as follows. Phthalylacetic acid (Neumann and Gabriel, *Ber.*, 1893, 26, 952) was reduced electrolytically to phthalideacetic acid (I). This was converted through its acid chloride into *phthalideacetamide*, which, when boiled in xylene solution with phosphorus pentoxide, lost water and gave *phthalideacetoneitrile* (II). The



lactone ring of this substance was opened on treatment with caustic soda, and by carefully heating the sodium salt in a vacuum *o*-carboxycinnamonitrile was produced.

If the acyl derivatives of 1-nitroso- $\beta$ -naphthol are heated at  $140^\circ$  for a short time, they will give the *o*-cyanocinnamic acid of m. p.  $255-256^\circ$  on hydrolysis.

The low-melting acid itself, when heated above its melting point for a few minutes, is completely converted into the high-melting *o*-cyanocinnamic acid. Since both cyano-acids on electrolytic reduction give  $\beta$ -*o*-cyanophenylpropionic acid (III), the only possible conclusion is that these acids are geometric isomerides similar to cinnamic and *allocinnamic* acids. On the analogy of these, the low-melting acid has been called *o*-cyano*allocinnamic* acid.

As  $\beta$ -*o*-cyanophenylpropionic acid was required in quantity, the most suitable conditions for its preparation were investigated. A method is described, using toluenesulphonyl chloride, which is suitable for large-scale preparations; about 6% of the acyl derivative



is hydrolysed to 1-nitroso- $\beta$ -naphthol, but this is easily separated owing to its insolubility in sodium carbonate solution.

Since in these reactions 1-nitroso- $\beta$ -naphthol obviously reacted in the oxime form, it seemed probable that substances containing the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  in a ring, if first converted into their isonitroso-derivatives, would react with acid chlorides in the same way. This was investigated in the case of the hydrindones. Hydrindone itself gave *o*-carboxyphenylacetonitrile in 92% yield, whilst 5:6-dimethoxy- and 5:6-methylenedioxy-hydrindones gave the corresponding cyano-acids. These three cyano-acids have recently been prepared by Haworth and Pink (J., 1925, 127, 1369) by the action of phosphorus pentachloride on the nitrosohydrindones. They easily decompose on warming, but by cautious treatment with thionyl chloride may be converted into their acid chlorides, from which their esters, amides, and substituted amides may be obtained.

#### EXPERIMENTAL.

*Action of Benzenesulphonyl Chloride upon 1-Nitroso- $\beta$ -naphthol.*—1-Nitroso- $\beta$ -naphthol (1 g.-mol.) is mixed with benzenesulphonyl chloride (1 g.-mol.), the whole is dissolved in the minimum quantity of cold acetone, and 8% caustic soda solution (1.2 g.-mols.) is added slowly, with shaking and cooling in ice. The *benzenesulphonyl-1-nitroso- $\beta$ -naphthol* that separates crystallises from a little acetone in yellow prisms, m. p. 124–125° (decomp.) (Found: C, 61.6; H, 3.6.  $\text{C}_{16}\text{H}_{11}\text{O}_4\text{NS}$  requires C, 61.3; H, 3.5%). On being kept at its m. p. for a few minutes, it resolidifies and thereafter melts at 137–139°, having been converted into an isomeride which crystallises from acetone in cream needles, m. p. 141° (Found: C, 61.7; H, 3.5%).

The low-melting acyl derivative is hydrolysed when dissolved in a slight excess of 8% caustic soda solution at 60°. The filtered cooled solution on acidification deposits *o*-cyanoallocinnamic acid in almost colourless needles. This crystallises from water, containing a little animal charcoal, in colourless, felted needles, m. p. 137° (Found: C, 69.7; H, 4.4. Calc. for  $\text{C}_{10}\text{H}_7\text{O}_2\text{N}$ : C, 69.4; H, 4.1%). When the benzenesulphonyl derivative, m. p. 141°, is treated in the same way, *o*-cyanocinnamic acid separates in a gelatinous form; it crystallises from glacial acetic acid in slightly brown, glistening plates, m. p. 256°, identical with the product of heating the sodium salt of 1-nitroso- $\beta$ -naphthol with sand at 180°.

*Direct Preparation of o-Cyanoallocinnamic Acid.*—A solution of 1-nitroso- $\beta$ -naphthol (43 g.) and toluenesulphonyl chloride (47 g.) in the minimum quantity of acetone is kept at 55–60° while caustic soda (8% solution) is added slowly, with constant shaking, so that

the solution is kept faintly alkaline. When the solution finally becomes permanently alkaline, it is cooled, filtered, and acidified, 38 g. of crude *o*-cyanallocinnamic acid being precipitated. For the preparation of *o*-cyanophenylpropionic acid further purification is unnecessary.

*o*-Carboxycinnamic acid, m. p.  $182^{\circ}$ , is produced when either of the *o*-cyanocinnamic acids is refluxed for 2 hours with 10% caustic soda solution, and is precipitated on acidification.

$\beta$ -*o*-Cyanophenylpropionic Acid (III).—A solution of crude *o*-cyanallocinnamic acid (40 g.) in 14% sodium carbonate solution (150 c.c.) is filtered from insoluble gummy impurities and reduced electrolytically for 3 hours at a lead cathode, the current density being 2 amps./100 sq. cm.; the anode cell consists of a lead electrode in 20% caustic soda solution. The product on acidification deposits a slightly brown, sandy powder, which crystallises from water in prisms, m. p.  $127^{\circ}$  (Found: C, 68.9; H, 5.0.  $C_{10}H_9O_2N$  requires C, 68.6; H, 5.2%).

*o*-Carboxycinnamonitrile,  $CO_2H \cdot C_6H_4 \cdot CH:CH \cdot CN$ .—Phthalyl-acetic acid (40 g.) dissolved in caustic soda (200 c.c. of 15% solution) is reduced electrolytically under the conditions described above. The hot solution is acidified with hydrochloric acid and filtered; on cooling, phthalideacetic acid separates in colourless plates, m. p.  $151^{\circ}$ , identical with the substance obtained by the reduction of phthalylacetic acid with sodium amalgam (Gabriel and Michael, *Ber.*, 1877, 10, 391). The acid (10 g.) is boiled with thionyl chloride (20 c.c.) for 15 minutes, the excess of thionyl chloride distilled away, the gummy residue dissolved in a little chloroform, and the solution slowly added to aqueous ammonia (60 c.c.;  $d$  0.880) cooled in ice, the temperature being kept below  $10^{\circ}$  during the addition. The chloroform is then evaporated on the water-bath; on cooling, phthalideacetamide separates in rectangular plates, m. p.  $182$ — $183^{\circ}$  (Found: N, 7.5.  $C_{10}H_9O_3N$  requires N, 7.3%). This amide (2 g.) is heated in boiling xylene (16 c.c.) with phosphorus pentoxide (4 g.) for 15 minutes. The boiling filtered xylene, on cooling, deposits pure white needles, m. p.  $111^{\circ}$ , of phthalideacetonitrile, and more may be obtained by extracting the brown, gummy residue from the xylene with boiling water, the latter depositing slightly brown needles on cooling. The nitrile is insoluble in cold alkali, but dissolves readily on warming, ammonia being evolved from the boiling solution.

A solution of phthalideacetonitrile in the theoretical quantity of warm caustic soda solution is evaporated to dryness on the water-bath, the residue kept at  $200^{\circ}$  in a vacuum for 10 minutes, cooled, and dissolved in water. On acidification a slightly yellow powder

separates which crystallises from water as a microcrystalline powder, m. p. 169—172° (Found: N, 7.3.  $C_{10}H_9O_3N$  requires N, 7.3%). This is *o*-carboxycinnamionitrile and yields *o*-carboxycinnamic acid, m. p. 182°, on hydrolysis (as above).

*o*-Carboxyphenylacetoneitrile.—2-isoNitroso-1-hydrindone (7.2 g.) is dissolved in caustic soda (80 c.c. of 8% solution), and benzenesulphonyl chloride (9 g.) added with constant shaking. The benzenesulphonyl derivative first separates as a white gum, which slowly dissolves on raising the temperature to 80° for a few minutes. The cooled filtered solution on acidification deposits *o*-carboxyphenylacetoneitrile as a white powder crystallising from water in colourless needles, m. p. 126°, identical with the substance obtained by Haworth and Pink (*loc. cit.*).

2-Carboxy-4 : 5-dimethoxyphenylacetoneitrile is obtained from dimethoxyisonitrosohydrindone (3 g.), caustic soda (3 g. in 25 c.c. of water), and benzenesulphonyl chloride (2.2 c.c.) by the method described above; it crystallises slowly in needles, m. p. 166—167°.

2-Carboxy-4 : 5-methylenedioxyphenylacetoneitrile, obtained in exactly the same way as the dimethoxy-compound, crystallises in slightly yellow prisms, m. p. 195° (Found: C, 58.3; H, 3.4. Calc., C, 58.5; H, 3.4%).

The author wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which covered the cost of the materials used in this investigation.

KING'S COLLEGE, LONDON.

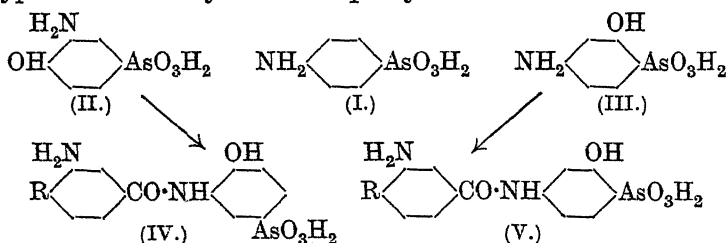
[Received, January 4th, 1926.]

## CXII.—Trypanocidal Action and Chemical Constitution. Part IV. Arylamides of Aminohydroxyphenylarsinic Acids.

By LESLIE FRANK HEWITT and HAROLD KING.

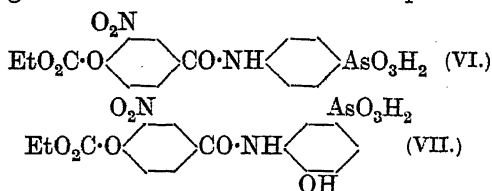
IN Parts I and II (King and Murch, J., 1924, **125**, 2595; 1925, **127**, 2632) the preparation and properties of a number of arylamides of 4-aminophenylarsinic acid (I) were described. Inasmuch as Fournneau and his colleagues (*Ann. Inst. Pasteur*, 1923, **37**, 551) have shown that on *Trypanosoma brucei* in mice, 3-amino-4-hydroxyphenylarsinic acid (II) and 4-amino-2-hydroxyphenylarsinic acid (III) with chemo-therapeutic indices (curative dose/tolerated dose) of 1/5 and 1/8 respectively are superior to 4-aminophenylarsinic acid with an index of 1/1, it was thought of interest to introduce into these hydroxy-acids certain substituted aminobenzoyl radicals

which were shown in Part II to have a favourable influence on the trypanocidal activity of 4-aminophenylarsinic acid.



The types (IV) and (V), where R is H, OMe, or OH, were obtained by reduction of the corresponding nitro-acids by ferrous chloride and alkali, the preparation of the nitrohydroxybenzoyl derivatives (R = OH) necessitating the use of ethylcarbonatonitrobenzoyl chloride, where the hydroxyl group is protected by the carbethoxyl group.

Although the ethylcarbonato-group in 3'-nitro-4'-ethylcarbonato-benzoyl-4-aminophenylarsinic acid (VI) is readily hydrolysed with negligible fission at the amide link by brief boiling with *N*-alkali (King and Murch, Part II), in the case of 3'-nitro-4'-ethylcarbonato-benzoyl-3-amino-4-hydroxyphenylarsinic acid (VII) hydrolysis of this group by cold *N*-alkali leads to appreciable fission of the amide link and much greater fission occurs on rise of temperature.



The maximum dose tolerated by mice, expressed in milligrams per gram of mouse, and the minimum curative dose, where determined, on an experimental infection of *T. equiperdum* in mice, of this group of twelve related compounds is shown below, R signifying the para-substituent to the amide group and *r* the number of days before relapse occurred.

Type IV. Derivatives of 3-NH<sub>2</sub>·4-OHC<sub>6</sub>H<sub>3</sub>·AsO<sub>3</sub>H<sub>2</sub>.

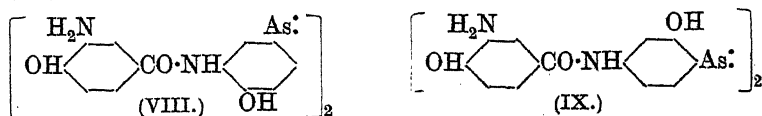
R .....	Nitro-acids.			Amino-acids.		
	H.	OMe.	OH.	H.	OMe.	OH.
Dosis tolerata .....	0.075	0.2	0.4	0.3	0.2	0.3
Dosis curativa ...	—	—	—	0.3	0.15	0.3
				( <i>r</i> = 13)	( <i>r</i> = 4)	( <i>r</i> = 8)

Type V. Derivatives of 4-NH<sub>2</sub>·2-OHC<sub>6</sub>H<sub>3</sub>·AsO<sub>3</sub>H<sub>2</sub>.

R .....	H.	OMe.	OH.	H.	OMe.	OH.
Dosis tolerata .....	0.2	0.2	0.3	0.1	0.6	0.2
Dosis curativa ...	—	—	—	0.1	0.3	0.2
				( <i>r</i> = 12)	( <i>r</i> > 30)	( <i>r</i> = 12)

On comparing these results with those obtained for the corresponding derivatives of 4-aminophenylarsinic acid (Part II) it will be observed that there is here no enhanced trypanocidal activity such as might be expected from the relative activities of the parent mono-nuclear arsenic acids (I, II, and III). There is, however, a rough parallelism between the activities of the amides of 4-aminophenylarsinic acid and those of 4-amino-2-hydroxyphenylarsinic acid; in each case, the aminoanisoyl derivative is the only one of the three amides with permanent curative properties.\* Expressed otherwise, one might say that the introduction of the 2-hydroxyl group into derivatives of 4-aminophenylarsinic acid has not radically altered the distribution of the main and residual affinities of the molecule on which trypanocidal activity as measured by the two determinants, curative dose and tolerated dose, ultimately depends.

The possession by the six complex amino-arsinic acids above described of a free hydroxyl group emphasised the desirability of the preparation of the corresponding arseno-derivatives, which like salvarsan should be administrable by solution in alkali. The comparison of six arseno-bases with the parent amino-acids was all the more a desideratum because Fournéau has expressed the opinion that on the evidence available the arsenic acids are at least as active as the arseno-derivatives. Unfortunately this object was only realisable in part because, unexpectedly, the possession of a single hydroxyl group in the same nucleus as the arseno-group did not confer alkaline solubility, the sodium salts of the aminobenzoyl and aminoanisoyl derivatives being quite insoluble in water. In addition, the hydroxyl group ortho to the arseno-group in derivatives of 4-amino-2-hydroxyphenylarsinic acid weakens the attachment of the arsenic atom to the nucleus, thus leading under very mild conditions of reduction by hypophosphorous acid to formation of products containing polyarsenides. This is perhaps not surprising, because the parent acid, 4-amino-2-hydroxyphenylarsinic acid, when reduced by the same reagent gives no arseno-base but only free arsenic. The hydroxyaminobenzoyl derivatives (VIII) and (IX) were, however, alkali-soluble, the former substance being of



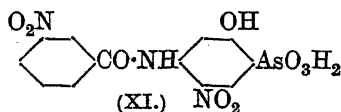
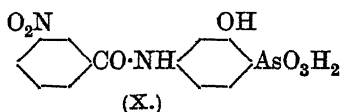
\* In this series of communications, the term "permanent curative property" indicates no relapse of some of the animals within 30 days, the blood being examined almost daily over that period. As a rule, each dose is tried on five mice.

special interest because of the duplication of the *o*-aminophenol grouping contained in salvarsan. The maximum tolerated and the minimum curative dose of these two arseno-bases in comparison with their parent arsenic acids are shown below.

	Acid.	Arseno (VIII).	Acid.	Arseno (IX).
<i>Dosis tolerata</i> .....	0.3	0.075	0.2	0.075
<i>Dosis curativa</i> .....	0.3	0.03	0.2	0.02
	( <i>r</i> = 8)	( <i>r</i> = 5)	( <i>r</i> = 12)	( <i>r</i> > 30)

Whilst there is little difference in activity between the arseno-derivative (VIII) and its parent acid, the arseno-derivative (IX) is permanently curative on one-fourth of its tolerated dose and is thus far superior to its parent acid. It should, however, be borne in mind that the arseno-derivative (IX) contains a certain proportion of polyarsenides, as has been indicated above.

3'-Nitrobenzoyl-4-amino-2-hydroxyphenylarsinic acid (X) on further nitration yields exclusively 3':5-dinitrobenzoyl-4-amino-2-hydroxyphenylarsinic acid (XI), which on reduction yields the corresponding diaminobenzoylamino-2-hydroxyphenylarsinic acid.



In Part II it was shown that the diamino-arsinic acids were in general permanently curative, but this substance, either on its maximum tolerated dose or on lower doses, was completely devoid of action. Various reasons might be advanced for this, but it is not proposed to discuss them here.

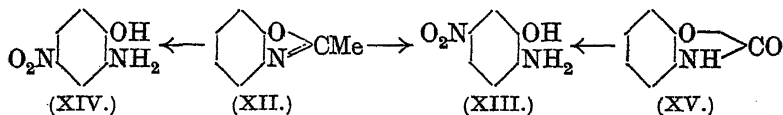
On hydrolysis of (XI) by alkali 5-nitro-4-amino-2-hydroxyphenylarsinic acid was obtained and this on reduction gave a new 4:5-diamino-2-hydroxyphenylarsinic acid of which only one isomeride is known. The activity of this diamino-acid in comparison with the closely related 4-amino-2-hydroxyphenylarsinic acid (III) and 3-amino-4-hydroxyphenylarsinic acid (II) is shown in the following table :

	Diamino-acid.	III.	II.
<i>Dosis tolerata</i> .....	0.3	0.5	1.5
<i>Dosis curativa</i> .....	0.05 ( <i>r</i> = 16)	0.2	0.3

The diamino-acid was very erratic in its curative action and far inferior to (II) or (III). It will be noticed that the indices for (II) and (III) are not as favourable on *T. equiperdum* as those obtained by Fourneau (see opening paragraph) on *T. brucei*.

4-Amino-2-hydroxyphenylarsinic acid (III), required in quantity in this investigation, was prepared by the Bart-Schmidt reaction from 5-nitro-2-aminophenol (Bauer, *Ber.*, 1915, 48, 1582). The

preparation of the latter from 2-aminophenol presents some points of interest to the student of orientation. Meldola and Wechsler (P., 1900, 180) showed that *ON*-diacetyl-2-aminophenol on attempted mononitration gave exclusively 4 : 6-dinitro-2-aminophenol (picramic acid) after hydrolysis, and we find in support that both mono- and tri-acetyl-2-aminophenol on mononitration yield after hydrolysis almost exclusively picramic acid, although in the case of triacetyl-2-aminophenol traces of both 5-nitro- and 4-nitro-2-acetylaminophenol have been isolated. In D.R.-P. 165650, however, 5-nitro-2-aminophenol is said to be prepared by the nitration of ethenyl-2-aminophenol (XII). An examination of this reaction shows that 5-nitro-2-aminophenol (XIII) is indeed formed together with 4-nitro-2-aminophenol (XIV) in the ratio 4 : 1, the main bulk of the 5-nitro-compound after hydrolysis being separable owing to its lesser solubility in water. The remaining mixture can be separated by fractionally crystallising the acetates from benzene, which obviates both the tendency of the two isomerides to separate from water as brilliant red mixed crystals and the formation of the low-melting hydrate of the 4-nitro-derivative.



The sulphonation product of carbonyl-2-aminophenol (XV) is known to yield 2-aminophenol-5-sulphonic acid on hydrolysis (D.R.-P. 197496; King, J., 1921, 119, 1117), but although 5-nitro-carbonyl-2-aminophenol is prepared by the action of nitric acid on carbonylaminophenol and yields nitrocatechol on alkaline hydrolysis (Chelmicki, *J. pr. Chem.*, 1890, 42, 441), there is no record of its hydrolysis by acids. This should also lead to the required 5-nitro-2-aminophenol. This has now been effected, but only with difficulty, as 5-nitrocarbonyl-2-aminophenol is very resistant to acid hydrolysis. Of the two possible routes to the required nitroaminophenol, the one *via* the ethenyl derivative proved the more convenient.

Thus, whilst the nitration of any of the acetyl derivatives of 2-aminophenol yields as main product picramic acid in which the orienting power of the hydroxyl may be said to overwhelm that of the acetylated amino-group in agreement with the behaviour of 4-aminophenol derivatives, in ethenyl- and carbonyl-aminophenol the reverse is true. The latter cases are also in agreement with the nitration of another cyclic derivative of 2-aminophenol, acetylphenoxazine, which yields 3 : 9-dinitrophenoxazine, the nitro-

groups entering the para-position to the nitrogen atom (Kehrmann and Saager, *Ber.*, 1903, **36**, 477).

To Miss F. M. Durham and Miss J. Marchal of this department we again tender our thanks for the efficient and painstaking care bestowed on the biological side of our subject.

#### EXPERIMENTAL.

*o*-Aminophenol.—The large quantities of *o*-aminophenol required were prepared in part by an improvement on Grandmougin's process (*Ber.*, 1906, **39**, 3561). *o*-Nitrophenol dissolved in 2*N*-sodium hydroxide (1 mol.) was treated with solid sodium hyposulphite (1.6 mols.) and sufficient sodium hydroxide to keep the reaction mixture faintly alkaline, the solution being well stirred and the temperature kept below 30°. The yield of *o*-aminophenol, including ether-extracted material, was 67%.

*Nitration of Ethenyl-o-aminophenol* (XII).—Ethenyl-*o*-aminophenol was obtained in 90% yield by a simplification of Ladenburg's method (*Ber.*, 1876, **9**, 1524). *o*-Aminophenol (carefully freed from inorganic salts) was distilled with 3 parts of acetic anhydride, and the distillate refractionated through a short column. The fraction, b. p. 200—210°, consisted of ethenyl-*o*-aminophenol. Of this, 53.9 g. were dissolved in sulphuric acid (200 c.c.) below 0° and treated with nitric acid ( $d$  1.42; 1.1 mols.) dissolved in an equal volume of sulphuric acid. On pouring on to ice, a bulky yellow compound was obtained, but attempts to isolate a pure nitroethenyl-*o*-aminophenol from this were unsuccessful. (When dried in a vacuum, it lost 90% of its weight and liquefied, and repeated crystallisation from alcohol gave eventually pure 5-nitro-2-acetylaminophenol.) The wet, bulky precipitate was heated at 100° with 325 c.c. of hydrochloric acid ( $d$  1.16) until dissolved, and the solution almost neutralised. Orange needles of 5-nitro-2-aminophenol (37.7 g.) separated immediately. On adjusting the reaction of the filtrate to neutrality, a red, crystalline solid (9.4 g.) separated which was almost pure 4-nitro-2-aminophenol. On one crystallisation from benzene with addition of glacial acetic acid, it yielded the pure *acetate*, yellow sheaves, which on drying at 95° gave 8.5 g. of the pure base. Ether extraction of the mother-liquors gave a semi-solid product which, fractionally crystallised as acetate from benzene and a little glacial acetic acid, gave further small quantities of 5-nitro-2-aminophenol (1.8 g.) and 4-nitro-2-aminophenol (3.0 g.). The total yield of pure nitroaminophenols was 83%.

5-Nitro-2-aminophenol (XIII) when quite pure melts at 203—204° and crystallises from water in orange or dark brown needles (Friedlaender and Zeitlin, *Ber.*, 1894, **27**, 192, give m. p. 201—202°).



This compound was also obtained as green plates, which melted at  $170^{\circ}$ , but crystallised almost instantaneously, and then melted at  $203\text{--}204^{\circ}$ . The velocity of transformation in contact with aqueous solutions is, however, slow. The *N*-monoacetyl derivative, obtained by the action of acetic anhydride without the application of heat, is sparingly soluble in boiling alcohol and crystallises in stout, pale yellow prisms, m. p.  $271\text{--}272^{\circ}$  (Found: C, 49.0; H, 4.1.  $\text{C}_8\text{H}_8\text{O}_4\text{N}_2$  requires C, 49.0; H, 4.1%). The ON-diacetyl derivative is formed very readily by boiling the aminonitrophenol with acetic anhydride. It is readily soluble in boiling alcohol and crystallises as a felt of fine needles, m. p.  $193\text{--}194^{\circ}$  (Found: C, 50.5; H, 4.3.  $\text{C}_{10}\text{H}_{10}\text{O}_5\text{N}_2$  requires C, 50.4; H, 4.2%). The triacetyl derivative was isolated from the acetylation mother-liquors of the preceding. It crystallises from absolute alcohol, in which it is readily soluble, in fern-like clusters of stout crystals, m. p.  $138\text{--}139^{\circ}$  (Found: C, 51.6; H, 4.5.  $\text{C}_{12}\text{H}_{12}\text{O}_6\text{N}_2$  requires C, 51.4; H, 4.3%).

4-Nitro-2-aminophenol (XIV) forms an *N*-monoacetyl derivative, m. p.  $279\text{--}280^{\circ}$ , by the action of acetic anhydride at room temperature. It forms clusters of needles from absolute alcohol, in which it is very sparingly soluble at the boiling point (Found: C, 48.9; H, 4.2.  $\text{C}_8\text{H}_8\text{O}_4\text{N}_2$  requires C, 49.0; H, 4.1%). The ON-diacetyl derivative, formed with difficulty by long boiling with excess of acetic anhydride, crystallises from boiling absolute alcohol, in which it is readily soluble, in needles or prisms, m. p.  $187\text{--}188^{\circ}$  (Found: C, 50.2; H, 4.3.  $\text{C}_{10}\text{H}_{10}\text{O}_5\text{N}_2$  requires C, 50.4; H, 4.2%).

*Nitration of Carbonyl-o-aminophenol (XV).*—Carbonyl-o-aminophenol (0.5 g.) was warmed with 2 c.c. of nitric acid (*d* 1.42); a violent reaction then occurred accompanied by frothing. The mononitro-compound crystallised out and was isolated by pouring into water. The yield was 0.5 g., m. p.  $255^{\circ}$  (Bender, *Ber.*, 1886, 19, 2271, gives m. p.  $256^{\circ}$ ). When boiled for 6 hours with 16% hydrochloric acid, it was for the most part undissolved and unchanged, but neutralisation of the filtrate and ether extraction gave 0.15 g. of 5-nitro-2-aminophenol, m. p.  $201^{\circ}$ . The unchanged residue was boiled with hydrochloric acid (32%) and alcohol for 8 hours and gave a portion of unchanged compound and 0.2 g. of 5-nitro-2-aminophenol.

*Nitration of N-Acetyl-2-aminophenol.*—On nitration with nitric acid (1 mol.) as described for ethenyl-2-aminophenol, the sole product obtained was 4:6-dinitro-2-acetylaminophenol (acetyl-picramic acid).

*Nitration of Triacetyl-2-aminophenol.*—When nitrated with nitric acid (1 mol.) as for the ethenyl derivative, this phenol yields small quantities of the monoacetyl derivatives of 4- and 5-nitro-2-amino-

phenol, readily isolated by reason of their sparing solubility in alcohol. If, however, the nitration product be hydrolysed, 4:6-dinitro-2-aminophenol (picramic acid) is readily isolated as the main product of the nitration.

**4-Amino-2-hydroxyphenylarsinic Acid (III).**—4-Nitro-2-hydroxyphenylarsinic acid was obtained in 78% yield from 5-nitro-2-aminophenol as described by Bauer (*loc. cit.*) except that the main bulk of arsenic acid separated on neutralisation to Congo-paper, without proceeding *via* the magnesium salt. On reduction with ferrous chloride by the method of Jacobs, Heidelberger, and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1580) it gives an 84% yield of 4-amino-2-hydroxyphenylarsinic acid. The *hydrochloride*, *nitrate*, and *sulphate* all crystallise from the corresponding *N*-acids in acicular crystals, and with the exception of the sulphate are readily soluble on warming. On addition of nitrite, a yellow colour is developed, and on adding to alkaline  $\beta$ -naphthol, a red colour is produced. The same colour is produced by pouring into alkali, probably through self-coupling. Addition of excess of nitrite destroys the coupling property almost instantaneously.

**3'-Nitrobenzoyl-4-amino-2-hydroxyphenylarsinic Acid (X).**—The *m*-nitrobenzoylation was carried out exactly as described for the isomeric 3-amino-4-hydroxyphenylarsinic acid, an 89% yield of the amide being obtained. It is almost insoluble in hot glacial acetic acid, but slightly soluble in hot 90% formic acid, from which it crystallises in bunches of needles (Found: As, 19.5.  $C_{13}H_{11}O_7N_2As$  requires As, 19.6%). The *sodium* salt crystallises in fine needles.

**3'-Aminobenzoyl-4-amino-2-hydroxyphenylarsinic Acid (V; R = H).**—This acid was prepared as described for the isomeric derivative of 3-amino-4-hydroxyphenylarsinic acid (*vide infra*) in 72% yield. Liberated from acid solution by sodium acetate, it separates micro-crystalline (Found: As, 20.8; 20.7.  $C_{13}H_{13}O_5N_2As$  requires As, 21.3%). The *sodium* salt crystallises in platelets, the *ammonium* salt as a felt of needles. The *hydrochloride*, clusters of needles, and *nitrate*, minute needles, are readily soluble in their respective warm *N*-acids, but the *sulphate*, clusters of needles, is rather sparingly soluble in boiling *N*-sulphuric acid.

The *arseno*-derivative prepared by the action of hypophosphorous acid at 60° contained 30% of As as against 24.8% (theoretical) and consisted therefore mainly of polyarsenides. It was insoluble in sodium hydroxide or mineral acids, but dissolved on adding nitrite.

**3':5-Dinitrobenzoyl-4-amino-2-hydroxyphenylarsinic Acid (XI).**—The above-described mononitro-acid (11.3 g.) was dissolved in sulphuric acid (45 c.c.), cooled to 0°, and nitrated with a mixture

of 2.15 c.c. of nitric acid ( $d$  1.42) and sulphuric acid (2 c.c.). On pouring on to ice, a yellow, microcrystalline precipitate separated. It was collected, dissolved in sodium carbonate, and reprecipitated by acid. The yield was 95% (Found: As, 17.7.  $C_{13}H_{10}O_9N_3As$  requires As, 17.6%). This acid is sparingly soluble in boiling acetic acid and crystallises in microscopic needles, more soluble in formic acid, from which it separates in much longer needles.

On hydrolysis by boiling with 15 volumes of *N*-sodium hydroxide for 40 minutes, it gave pure *m*-nitrobenzoic acid, and 5-nitro-4-amino-2-hydroxyphenylarsinic acid, short, yellow prisms crystallising readily from hot water, in which it is fairly readily soluble. It is sparingly soluble in 3*N*-hydrochloric acid, but readily soluble in concentrated acid. It diazotises with nitrite and thereafter couples with alkaline  $\beta$ -naphthol. Excess of nitrite, however, destroys the coupling property (Found: As, 27.1.  $C_6H_7O_6N_2As$  requires As 27.0%).

3' : 5-Diaminobenzoyl-4-amino-2-hydroxyphenylarsinic Acid.—This was obtained in 71% yield by reduction of the dinitro-acid with ferrous chloride and alkali. When liberated from the alkaline extracts of the ferric hydroxide, it separates in very fine needles, but occasionally as an amorphous, voluminous solid which becomes crystalline on warming the precipitation liquor (Found: As, 20.6.  $C_{13}H_{14}O_5N_3As$  requires As, 20.4%). The hydrochloride is very soluble in *N*-hydrochloric acid, but separates from stronger acid in narrow leaflets with domed ends; the sulphate, minute needles, is only moderately soluble in *N*-sulphuric acid, but the nitrate is very readily soluble in *N*-nitric acid and crystallises from more concentrated acid in needles and in lenticular prisms. On addition of nitrite, it diazotises and then gives the same red colour on pouring into alkali, probably owing to self-coupling, as on adding to alkaline  $\beta$ -naphthol. This acid is very resistant to hydrolysis. It is unchanged after boiling with *N*-alkali for an hour, or after 7 hours' boiling with concentrated hydrochloric acid. It was recovered to the extent of more than 60% after 5 hours' heating with concentrated hydrochloric acid under pressure at 150°. *m*-Aminobenzoic acid was identified as a hydrolytic product.

4 : 5-Diamino-2-hydroxyphenylarsinic Acid.—5-Nitro-4-amino-2-hydroxyphenylarsinic acid (2.0 g.) was dissolved in 22 c.c. of *N*-sodium hydroxide (3 mols.) at 0° and to the vigorously stirred solution were added all at once 5.0 g. of sodium hyposulphite (1 mol. of 80% = 4.7 g.) with removal of the external bath. After being stirred for 2 hours, the solution was filled with fine needles of the required amino-acid. This was collected and washed with ice-cold water (yield 93%). For analysis and physiological testing, it was

dissolved in 20 c.c. of 0.7*N*-hydrochloric acid and reprecipitated by addition of saturated sodium acetate. On 1.65 g. there was a loss of 0.1 g. The *diamino-acid* crystallises from boiling water, in which it is sparingly soluble, in fine needles. It is very soluble in *N*-hydrochloric acid and gives, on addition of nitrite, a red coloration, which becomes pale after a few seconds. This is followed by separation of the *diazoimine*, in rectangular leaflets. The diamino-acid reduces ammoniacal silver nitrate instantly at room temperature. In acid solution, potassium dichromate gives a port wine colour (Found : As, 29.0.  $C_6H_9O_4N_2As \cdot \frac{1}{2}H_2O$  requires As, 29.0%).

*3'-Nitroanisoyl-4-amino-2-hydroxyphenylarsinic Acid*.—Prepared in 83% yield in the same way as its isomeride (*vide infra*), this acid is almost insoluble in hot glacial acetic acid, but crystallises from hot 90% formic acid in spear-shaped needles (Found : As, 18.4.  $C_{14}H_{13}O_5N_2As$  requires As, 18.2%). The *sodium* salt, silky needles, and *ammonium* salt, diamond-shaped plates, were only moderately soluble in water.

*3'-Aminoanisoyl-4-amino-2-hydroxyphenylarsinic Acid* (V; R = OMe).—This acid, obtained in 77% yield by reduction of the nitro-acid with ferrous chloride and alkali at 0°, separates as a jelly on acidification of the alkaline extracts of the ferric hydroxide. It soon crystallises, however, in silky needles (Found : As, 19.4.  $C_{14}H_{15}O_6N_2As$  requires As, 19.6%). The *sodium* salt crystallises in prisms readily soluble in water. The *hydrochloride*, spiked leaflets, is readily soluble in warm *N*-hydrochloric acid, but the *sulphate*, short, white needles and stout prisms, and *nitrate*, soft, woolly needles, are much less soluble in the warm *N*-acids.

The *arseno-base* could not be obtained sufficiently pure for physiological testing. Reduction with hypophosphorous acid under the mildest conditions gave polyarsenides containing between 26% and 56% of arsenic as against 22.6% required by theory. Reduction with hyposulphite even at 70° gave no trace of *arseno-base*.

*3'-Nitro-4'-ethylcarbonatobenzoyl-4-amino-2-hydroxyphenylarsinic Acid*.—3-Nitro-4-ethylcarbonatobenzoyl chloride (28.2 g.; 2 mols.) was added in several portions to 4-amino-2-hydroxyphenylarsinic acid (12 g.), dissolved in 2*N*-sodium hydroxide (45 c.c.), saturated sodium acetate solution (50 c.c.), and water (20 c.c.), with vigorous shaking. The reaction mixture was acidified to Congo-paper, and the precipitate collected after being well washed with dilute acid and water. When dry, it was extracted in a Soxhlet apparatus with ether and reprecipitated from sodium carbonate solution by acid. The yield was 73% of the theoretical. This acid is practically insoluble in hot glacial acetic acid, but separates from 90% formic

acid in microscopic, fluffy needles (Found : As, 15.9.  $C_{16}H_{15}O_{10}N_2As$  requires As, 15.9%).

*3'-Nitro-4'-hydroxybenzoyl-4-amino-2-hydroxyphenylarsinic Acid*.—The preceding acid (18.5 g.) was dissolved in 4 equivalents of *N*-sodium hydroxide (158 c.c.) and kept at room temperature for 18 hours. On acidification carbon dioxide and ethyl alcohol were liberated and a white, microcrystalline precipitate was thrown down. This was collected, dried, and extracted with ether in a Soxhlet apparatus (yield 89%). This acid dissolves in alkali with a bright yellow colour, is almost insoluble in warm acetic acid, but crystallises from 90% formic acid in microscopic needles (Found : As, 18.8.  $C_{13}H_{11}O_8N_2As$  requires As, 18.8%).

*3'-Amino-4'-hydroxybenzoyl-4-amino-2-hydroxyphenylarsinic Acid* (V; R = OH).—Reduced as described for its isomeride (*vide infra*), this acid was obtained in 76% yield. Liberated from alkaline solutions by acid, it separates in a gelatinous condition, but rapidly crystallises, on warming, in elongated leaflets (Found : As, 20.0.  $C_{13}H_{13}O_6N_2As$  requires As, 20.4%). The *hydrochloride*, small needles, is readily soluble in *N*-hydrochloric acid; the *nitrate*, diamond-shaped plates, is sparingly soluble in hot *N*-nitric acid, and the *sulphate*, needles, is moderately soluble in warm *N*-sulphuric acid. On adding nitrite to a salt with mineral acids, a very sparingly soluble yellow *diazo-oxide* is precipitated, of amorphous appearance, but microscopically anisotropic. It couples intensely with alkaline  $\beta$ -naphthol.

*3'-Amino-4'-hydroxybenzoyl-4-amino-2-hydroxyarsenobenzene* (IX).—The above-described arsinic acid (3 g.) was suspended in 15 c.c. of hypophosphorous acid (*d* 1.14), diluted with an equal volume of water, and stirred at 45° for 2½ hours after addition of a crystal of potassium iodide. The orange-yellow arsenohypophosphite was worked up as described for aminobenzoyl-3-amino-4-hydroxy-arsenobenzene. The yield was 1.0 g. When dried, it formed a brittle, brownish-yellow powder, instantly soluble in sodium hydroxide to a pale yellow solution. It was not soluble in mineral acids, but dissolved on adding nitrite and then coupled with alkaline  $\beta$ -naphthol. On analysis, the product proved to contain polyarsenide (Found : As, 28.7.  $C_{26}H_{22}O_6N_4As_2$  requires As, 23.6%). When prepared at 55°, the proportion of polyarsenide was increased, as the arsenic content was 29.8%.

*3'-Nitrobenzoyl-3-amino-4-hydroxyphenylarsinic Acid*.—To a solution of 3-amino-4-hydroxyphenylarsinic acid (7.4 g.) in 2*N*-sodium hydroxide (25 c.c.) and half-saturated sodium acetate solution (200 c.c.) was added 3-nitrobenzoyl chloride (11.8 g.) dissolved in ether. The mixture was vigorously shaken, and sodium

hydroxide solution run in from time to time to maintain a slight alkalinity to phenolphthalein. On completion of the reaction, the mixture was made neutral to Congo-paper, the precipitated solid collected, washed with dilute acid, and, after drying, extracted thoroughly with ether. It was dissolved in alkali, reprecipitated by acid, dried, and again extracted with ether. The yield was 90%. This nitro-acid is almost insoluble in hot glacial acetic acid, but crystallises from hot 90% formic acid in silky needles (Found: As, 19.6.  $C_{13}H_{11}O_7N_2As$  requires As, 19.6%). The *ammonium* salt is sparingly soluble and crystallises in tufts of needles.

*3'-Aminobenzoyl-3-amino-4-hydroxyphenylarsinic Acid* (IV; R = H).—The nitro-acid (7.6 g.) was dissolved in 72 c.c. of 2*N*-sodium hydroxide solution at 0°, and ferrous chloride (28 g.) dissolved in 40 c.c. of water run in slowly with vigorous stirring. A further quantity (72 c.c.) of 2*N*-sodium hydroxide was then run in under the same conditions. After stirring for 90 minutes, the ferric hydroxide was filtered off and extracted twice by thorough disintegration with 150 c.c., each time, of 0.5*N*-sodium hydroxide. The combined alkaline filtrates were neutralised to Congo-paper, and the crystalline precipitate was collected. It was dissolved in 150 c.c. of *N*-hydrochloric acid and reprecipitated by addition of saturated sodium acetate solution. The yield was 44%. This amino-arsinic acid, so prepared, separates in microscopic platelets of indefinite shape (Found: loss at 100°, 4.9, 4.7, 5.1.  $C_{13}H_{13}O_5N_2As \cdot H_2O$  requires  $H_2O$ , 4.9%. Found in anhydrous material: As, 20.8.  $C_{13}H_{13}O_5N_2As$  requires As, 21.3%). It is readily soluble in warm *N*-mineral acids, the *hydrochloride* crystallising in microscopic, narrow leaflets, the *sulphate* in rectangular leaflets, and the *nitrate* in microscopic plates.

*3'-Aminobenzoyl-3-amino-4-hydroxyarsenobenzene*.—The corresponding arsinic acid (1 g.) was suspended in a mixture of 30% hypophosphorous acid (5 c.c.), glacial acetic acid (5 c.c.), and water (5 c.c.), with addition of a crystal of potassium iodide. After stirring for 2 hours at 57°, the orange-yellow solid was centrifuged off, and the deposit washed several times with boiled-out water. It was then made alkaline by addition of aqueous sodium hydrogen carbonate and washed free from alkali by repeated centrifuging with water. The product was dried in a vacuum (yield 0.53 g.). This arsenobenzene is insoluble in aqueous acids or alkalis, but soluble in warm 90% formic acid. In acid solution, it dissolves immediately on addition of nitrite and then couples with alkaline  $\beta$ -naphthol with a deep red colour (Found: As, 24.8.  $C_{26}H_{22}O_4N_4As_2$  requires As, 24.8%).

*3'-Nitroanisoyl-3-amino-4-hydroxyphenylarsinic Acid*.—This acid

was obtained in 80% yield by the same process as is described for the corresponding 3'-nitrobenzoyl derivative. It is practically insoluble in boiling glacial acetic acid, but crystallises from 90% formic acid in square leaflets (Found: As, 17.9.  $C_{14}H_{13}O_8N_2As$  requires As, 18.2%). The *sodium* salt, acicular crystals, is readily soluble in water.

*3'-Aminoanisoyl-3-amino-4-hydroxyphenylarsinic Acid* (IV; R = OMe).—The reduction of the nitro-compound was carried out precisely as described for the preparation of the 3'-aminobenzoyl compound. The yield was 61%. Liberated from acid solution by sodium acetate, this acid crystallises in colourless plates (Found: As, 20.0.  $C_{14}H_{15}O_6N_2As$  requires As, 19.6%). The *hydrochloride*, rosettes of needles, is readily soluble in hot *N*-hydrochloric acid, the *sulphate*, microscopic, square leaflets, is less soluble in hot *N*-sulphuric acid, and the *nitrate*, long, silky needles, is sparingly soluble in hot *N*-nitric acid.

*3'-Aminoanisoyl-3-amino-4-hydroxyarsenobenzene*.—Prepared in the same way as the previously described arsenobenzene in 77% yield, this is a yellow powder insoluble in acids or alkalis, but instantly soluble in acid solution on addition of nitrite. It then couples with alkaline  $\beta$ -naphthol (Found: As, 22.7.  $C_{28}H_{26}O_6N_4As_2$  requires As, 22.6%).

*3'-Nitro-4'-ethylcarbonatobenzoyl-3-amino-4-hydroxyphenylarsinic Acid* (VII).—3-Amino-4-hydroxyphenylarsinic acid (11.6 g.) was dissolved in 100 c.c. of water with addition of 5.3 g. (2 mols.) of sodium carbonate. After addition of 100 c.c. of saturated sodium acetate solution, 27.3 g. (2 mols.) of 3-nitro-4-ethylcarbonatobenzoyl chloride were added in three portions with a few c.c. of ether, and well shaken. After  $\frac{1}{2}$  hour, the solution was made definitely acid to Congo-paper, and the mixture of acids collected, dried, and divided by ether extraction into 17.0 g. of the required arsinic acid, insoluble in ether, and 16.0 g. of recovered nitroethylcarbonatobenzoic acid, soluble in ether. This arsinic acid is readily soluble in cold 90% formic acid and crystallises therefrom in microscopic needles; from glacial acetic acid, in which it is readily soluble when hot, it separates either as needles or rectangular leaflets (Found: As, 16.1.  $C_{16}H_{15}O_{10}N_2As$  requires As, 15.9%).

*3'-Nitro-4'-hydroxybenzoyl-3-amino-4-hydroxyphenylarsinic Acid*.—The foregoing ethylcarbonato-acid (10 g.) was dissolved in *N*-sodium hydroxide (4 mols.) and kept for a day. It was diluted with an equal volume of water and precipitated with concentrated hydrochloric acid. On warming the mixture, the precipitated acid became partly crystalline. The dried acid, when extracted with ether to remove hydroxynitrobenzoic acid, was obtained in 84% yield. The

aqueous mother-liquors, extracted with ether, gave nitrohydroxybenzoic acid and also contained 3-amino-4-hydroxyphenylarsinic acid, as was proved by its coupling strongly with alkaline  $\beta$ -naphthol after diazotisation. The required arsinic acid dissolves in alkali with a bright yellow colour. It crystallises in diamond-shaped spicules from either boiling glacial acetic acid, in which it is sparingly soluble, or boiling 90% formic acid, in which it is readily soluble (Found: As, 19.2.  $C_{13}H_{12}O_6N_2As$  requires As, 18.8%).

*3'-Amino-4'-hydroxybenzoyl-3-amino-4-hydroxyphenylarsinic Acid.* (IV; R = OH).—The nitro-acid (8.8 g.) was dissolved in 33 c.c. of water with the aid of two equivalents (23 c.c.) of 2*N*-sodium hydroxide, and ferrous chloride (31 g.) in 42 c.c. of water added slowly with vigorous stirring at  $-5^\circ$ . Sufficient sodium hydroxide (167 c.c. of 2*N*) was now slowly added to make the reaction of the fluid distinctly alkaline to litmus. The filtered ferric hydroxide was thoroughly extracted, each time, with 170 c.c. of 0.2*N*-sodium hydroxide. On rendering the combined extracts neutral to Congo-paper, a copious separation of crystalline amino-acid ensued. This was purified by solution in 100 c.c. of *N*-nitric acid at  $50^\circ$  and precipitation with sodium acetate, and gave 4.0 g. The main mother-liquors were rapidly concentrated below  $50^\circ$  to a small volume and gave a mixture of the amino-compound and the corresponding azoxy-compound, readily separable by dilute nitric acid into 0.75 g. of azoxy-compound (9% yield) and 1.0 g. of amino-compound. The total yield of amino-compound was 62% (Found: As, 20.4.  $C_{13}H_{13}O_6N_2As$  requires As, 20.4%). The amino-acid diazotises with production of a deep yellow solution, from which an insoluble *diazo-oxide* crystallises in dense clusters of needles. It couples readily with alkaline  $\beta$ -naphthol. The *hydrochloride*, microscopic needles, is very sparingly soluble in boiling *N*-hydrochloric acid; the *sulphate*, leaflets, is sparingly soluble in warm *N*-sulphuric acid; and the *nitrate*, microscopic needles, is readily soluble in warm *N*-nitric acid.

The *azoxy*-compound crystallises very readily from boiling 90% formic acid, in which it is readily soluble, in pale brown, truncate, diamond-shaped plates. It dissolves in ammonia with a pale yellow colour and gives an insoluble magnesium salt on addition of magnesium chloride.

*3'-Amino-4'-hydroxybenzoyl-3-amino-4-hydroxyarsenobenzene* (VIII) was obtained in quantitative yield, allowing for recovered acid, by reduction of the corresponding acid (4.0 g.) with 20 c.c. of hypophosphorous acid ( $d$  1.14), 20 c.c. of water, 10 c.c. of acetic acid, and a crystal of potassium iodide at  $50-55^\circ$  for 3 hours. The pure arseno-base was isolated as described for the preceding members.



It is a yellow powder soluble in caustic alkalis, but forming insoluble orange salts with acids. It is instantly soluble to a yellow solution on addition of nitrous acid. From more concentrated solutions, the amorphous *diazo-oxide* separates; this couples with alkaline  $\beta$ -naphthol (Found: As, 23.8.  $C_{26}H_{22}O_6N_4As_2$  requires As, 23.6%).

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### CXIII.—*Liquid-line Corrosion.*

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THERE are many instances of enhanced corrosion occurring at the liquid line, when a solid is partly immersed in a liquid which has a chemical action on it, or which simply dissolves it. The phenomenon was first described by Spring (*Z. physikal. Chem.*, 1889, 4, 658) for calcite dissolving in hydrochloric acid and for sucrose and sodium carbonate dissolving in water. He concluded that the extra dissolution was due to an enhanced reactivity of the solvent at the surface. This explanation was denied by Klobukow (*ibid.*, 1890, 5, 180), who suggested that the greater portion of the solid was protected by the downward streaming of the product, whilst fresh solvent was always being drawn in at the liquid surface. Ganguly and Banerji (*Z. anorg. Chem.*, 1922, 124, 140) believe that the phenomenon is related to the surface tension of the liquid, since the effect was diminished in the cases they investigated by covering with a layer of oil.

The water-line corrosion of metals offers a special case of great practical importance. Here it is generally held that atmospheric oxygen assists in the corrosion near the surface of the liquid. Evans (compare "Corrosion of Metals," Arnold, 1924, p. 106) takes a more definite point of view and ascribes the effect to the automatic removal of ions from the metal in the vicinity of the water line, through the relatively cathodic nature of the portion above. Watson and Watts (*Trans. Amer. Electrochem. Soc.*, 1923, 44, 1) investigated many cases of slow corrosion of metals in aqueous solution and concluded that the effect was due to protection of the rest of the metal through the downward flow of the reaction products.

#### EXPERIMENTAL.

During the course of several years' work on the dissolution of metals in various reagents the author has been continually confronted with this phenomenon, and has had opportunities of studying

it, where the reaction velocity is fairly rapid. These seem to be more suitable and trustworthy conditions than the slow corrosion over periods of several weeks previously investigated.

Strips of zinc and magnesium were partially immersed in *N*-hydrochloric acid. The strips were eaten through along a line about 0.5 mm. above the water line some considerable time before the rest of the metal dissolved. Owing to the vigorous evolution of hydrogen, the reaction products were washed in an upward direction instead of downward, and the effect cannot be due in this case to protection of the metal thereby. Watson and Watts (*loc. cit.*) state that water-line corrosion does not take place when zinc dissolves in hydrochloric acid with disengagement of hydrogen. This statement, however, must be due to error of observation.

The effect has also been repeatedly obtained in the dissolution of magnesium in ammonium chloride solution, dilute sulphuric acid and dilute nitric acid, with zinc in dilute sulphuric acid and dilute nitric acid, and with aluminium in solutions of caustic soda and hydrochloric acid. Scarcely any effect was observed in the dissolution of iron in hydrochloric acid.

In all these cases the rate of gassing was sufficient to prevent any downward streaming of the reaction products. It seemed possible, however, that the depolarising action of oxygen contained in the surface of the solution could account for the increased velocity of corrosion. The experiments were therefore repeated in an atmosphere of hydrogen. Identical results were obtained, and thus it is established that the water-line corrosion of metals occurs in absence of the two causes which have been discussed.

Further evidence against the necessity for oxygen is furnished by the strong preferential liquid-line corrosion when strips of copper or iron are partly immersed in strong solutions of nitric acid. Here, the solution itself is a much more active depolariser than atmospheric oxygen. Again, although iron was not observed to undergo appreciable extra corrosion at the water line in hydrochloric acid, the effect is very marked when a mixture of hydrochloric and nitric acids is used. An idea of the magnitude of the effect is gained from an experiment in which copper sheet 0.022 inch in thickness dissolved in a mixture of 25 c.c. of nitric acid, 10 c.c. of hydrochloric acid, and 65 c.c. of water. When the water line was completely cut through, the thickness of the undissolved metal was 0.010 inch.

The excessive corrosion takes place just above the water line, at the place where a film of liquid creeps up the metal, and it seems that the increased velocity of reaction is a property of this film. Further evidence supporting this suggestion is gained from some observations on the dissolution of magnesium and zinc in dilute

acids. At suitable rates of reaction the ascending bubbles of hydrogen coalesce near the end of their course, forming a large bubble on either side of the metal sheet just under the water line. The bubble bursts in a short time, but is immediately formed again. Thus, during the greater part of the reaction, there exists just below the water line a thin film of solution in contact with the metal and bounded by the large bubble of hydrogen. Subsequent examination of the metal showed in every case a roughly circular patch indicative of strong preferential corrosion in the region adjacent to the bubble.

This explanation appears to account for the observation by McCulloch (*J. Amer. Chem. Soc.*, 1925, 47, 1940) that when a rubber band is wrapped tightly round a piece of iron which is then immersed in dilute hydrochloric acid, the iron is strongly corroded under the rubber band.

The author has also repeated Spring's experiment, dissolving sticks of marble in 0.5*N*-hydrochloric acid and in *N*-nitric acid. Under these conditions, the upward wash of carbon dioxide bubbles causes a visible upward streaming of the soluble product, which can be observed to fall subsequently down the sides of the vessel. Excessive corrosion at the water line occurred in both cases. Here the oxygen theory or the electrolytic theory cannot enter. Gurwitsch also (*Z. physikal. Chem.*, 1924, 109, 375) has performed experiments where the product of solution is specifically lighter than the solvent and yet found increased activity at the surface of the solution.

In experiments where little or no gas evolution occurred and the reaction products were allowed to flow down the metal, the effect was quite different when the metal broke off at the water line. The piece of metal was found to be progressively thinned from the bottom to the water line, resembling a fine wedge. In the other cases, where downward streaming was prevented, the fallen metal was of uniform thickness as though it had been sawn.

Whilst it may be admitted that the downward streaming of reaction products and depolarisation by oxygen may assist in preferential corrosion at the liquid line in suitable circumstances, these experiments indicate that the phenomenon takes place in absence of these causes, thus supporting the original hypothesis of Spring.

# CXIV.—*Observations on Liquid Boundaries and Diffusion Potentials.*

By SYDNEY RAYMOND CARTER and FREDERICK MEASHAM LEA.

DURING an investigation (J., 1925, 127, 487, 499) on the *E.M.F.* of systems involving potassium chloride and concentrated acid solutions, it was necessary to set up chains of connecting solutions having potentials which would be readily reproducible and be subject to the minimum fluctuation with time.

Various types of liquid junctions were studied, therefore, and the main results are collected in this paper. Thus in making up the oxidation cell (Pt)|Oxid. salts,  $xN\text{-HCl}|(a) \dots (b)$   $N\text{-KCl}, \text{Hg}_2\text{Cl}_2|\text{Hg}$  or (Pt)|Oxid. salts,  $xN\text{-HCl}|(a) \dots (b)$   $N\text{-H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4|\text{Hg}$  the chain  $xN\text{-HCl}|(a) \dots (b)|N\text{-KCl}$  or  $xN\text{-HCl}|(a) \dots (b)|N\text{-H}_2\text{SO}_4$  may be completed by connecting the points (a) and (b) in one of the following ways, (i) directly, (ii) through *N*-hydrochloric acid, (iii) through saturated potassium chloride solution.

A. *Acid-Acid Boundaries of the Type  $xN\text{-HCl}|N\text{-HCl}$ .*—This type of boundary occurred in scheme (ii), and two modes of formation of this boundary will be described.

(1) The connecting tube from (a) carries a tap and dips into hydrochloric acid of the same concentration ( $xN\text{-HCl}$ ). Connexion is made to a vessel containing *N*-hydrochloric acid by means of an inverted U tube filled with *N*-hydrochloric acid and, as in other cases, plugged at the ends with filter-paper. It makes but little difference, however (about 0.001 volt), if this connecting tube be filled with the  $xN$ -hydrochloric acid. Diffusion potentials at boundaries so set up show little fluctuation with time.

(2) If the open end of the tube with tap from (a) is immersed directly in *N*-hydrochloric acid, complete mixing of the two acid solutions takes place as far as the tap and it is here that the actual liquid junction occurs. If the  $xN$ -hydrochloric acid be 5*N*, this method gives diffusion potentials differing by about 0.006 volt from those obtained by method A (1).

In the work on the cupric-cuprous potentials, as well as that on the diffusion potentials, method A (1) was invariably employed.

B. *Acid-Salt Boundaries of the Type  $\text{HCl}|\text{KCl}$ .*—(1) Direct connexion between  $xN$ -hydrochloric acid and *N*-potassium chloride is equivalent to scheme (i) and leads to considerable fluctuations of *E.M.F.* when the value of  $x$  is high.

(2) An intermediate solution of *N*-hydrochloric acid between the

two solutions in (1) gives the combination  $xN\text{-HCl}|N\text{-HCl}|N\text{-KCl}$ , which is scheme (ii).

The  $xN\text{-HCl}|N\text{-HCl}$  boundary has already been described, and the  $N\text{-HCl}|N\text{-KCl}$  boundary is made as follows. The connecting tube is filled with  $N$ -potassium chloride, in which case the diffusion potential is constant to about 0.0010 to 0.0015 volt on standing. If the connecting tube be filled with  $N$ -hydrochloric acid, a divergence of about 0.002 volt from the above is observed. Our practice has been to use the potassium chloride solution.

Methods B (1) and (2) give values which differ considerably for the total diffusion potential between  $xN$ -hydrochloric acid and  $N$ -potassium chloride. For very strong hydrochloric acid solutions (10*N*—11*N*) this difference may amount to as much as 0.020 volt.

*C. Saturated Potassium Chloride Solutions.*—The interposition of a saturated potassium chloride solution between  $xN$ -hydrochloric acid and  $N$ -potassium chloride reduces the diffusion potential, but does not eliminate it completely for strong hydrochloric acid solutions. For concentrations of hydrochloric acid up to  $N$ , the conclusion of various workers is that saturated potassium chloride has no diffusion potential against the hydrochloric acid; but this does not hold for stronger hydrochloric acid solutions. Thus between 9*N*-hydrochloric acid and  $N$ -potassium chloride the interposition of a saturated potassium chloride solution reduces the diffusion potential from approximately 0.090 volt to 0.050 volt. A direct connexion  $xN\text{-HCl}|N\text{-KCl}$  always gives a lower diffusion potential than that obtained when an intermediate  $N$ -hydrochloric acid is introduced; for 9*N*-hydrochloric acid it is about 0.015 volt lower.

For 9*N*-hydrochloric acid the approximate values of the following diffusion potentials are:  $xN\text{-HCl}|N\text{-KCl}$ , 0.090 volt;  $xN\text{-HCl}|N\text{-HCl}|N\text{-KCl}$ , 0.105 volt;  $xN\text{-HCl}|\text{Sat. KCl}|N\text{-KCl}$ , 0.050 volt.

*D. Liquid Junctions with Sulphuric Acid of the Type  $xN\text{-HCl}|N\text{-H}_2\text{SO}_4$ .*—Very little difference is observed if direct connexion be made between the  $xN$ -hydrochloric acid and  $N$ -sulphuric acid or  $N$ -hydrochloric acid be interposed, giving the  $xN\text{-HCl}|N\text{-HCl}|N\text{-H}_2\text{SO}_4$  combination.

*Variation of Diffusion Potentials.*—For corresponding concentrations, an acid|salt boundary shows more variation with time than an acid|acid boundary. The latter, even for  $N$ -hydrochloric acid against 10*N*-hydrochloric acid, shows little variation, in general not more than 0.001 volt and usually less. If, however, the  $xN$ -hydrochloric acid contains a high concentration of some salt in solution, then the  $xN\text{-HCl}|N\text{-HCl}$  boundary may show a fluctuation of several millivolts.

In making potential measurements, the most consistent results were obtained when fresh boundaries were used wherever possible, and this is the experience of other workers.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of them (F.M.L.) which has enabled this investigation to be carried out.

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### CXV.—*The Hydrolytic Action of Low-pressure Superheated Steam on Salts of the Alkaline-earth Metals.*

By PERCY LUCOCK ROBINSON, HAROLD CECIL SMITH, and  
HENRY VINCENT AIRD BRISCOE.

ALTHOUGH it is generally realised that many salts are attacked by steam at high temperatures, and it is well known, as an extreme case, that salts like magnesium chloride are largely hydrolysed at temperatures little above the boiling point of water, there is little definite information in the literature as to the general incidence and extent of the hydrolytic action of steam. The recognition that many chlorides and bromides could thus be decomposed, even by the relatively low concentration of steam formed during their dehydration, led to the general use of the well-known Harvard bottling apparatus in atomic weight determinations, but it is in relation to technical processes of thermal decomposition that most references to such phenomena are found, and the following notes indicate their general nature.

The thermal decomposition of witherite is facilitated by the presence of steam (Priestley, *Phil. Trans.*, 1788, 78, 852; Lenoir, *Jahresber.*, 1867, 13, 256; Heinz, *Chem. News*, 1902, 85, 206) and a similar result is observed, apparently, when mixtures of barium carbonate with calcium carbonate and carbon (Jacquelin, *Compt. rend.*, 1851, 32, 877), and with sodium carbonate (*Dingler's Jour.*, 1884, 254, 436), are employed.

A patented process describes the hydrolytic decomposition of barium sulphide by steam (Leroy and Segay, D.R.-P. 100969, 1897). Fremy stated that fluorspar is decomposed by steam at a red heat, yielding calcium oxide and hydrogen fluoride (*Ann. Chim. Phys.*, 1856, 47, 17), but Poulenc later found that strontium fluoride is not decomposed by steam at a red heat (*ibid.*, 1894, 2, 5). It has been reported (Kunheim, "Über Einwirkung des

Wasserdampfes auf Chlormetalle bei hoher Temperatur," Gottingen, 1861) that when calcined in steam calcium chloride is decomposed less readily than magnesium chloride, but more readily than barium chloride, that this hydrolysis of calcium chloride is incomplete (Pelouze, *Compt. rend.*, 1861, **32**, 1267), and that it is accelerated when silica, alumina, or china clay are present (Solvay, *Dingler's Jour.*, 1885, **255**, 307).

When steam is passed over a red hot mixture of calcium sulphate and sodium chloride, sodium sulphate, lime and hydrogen chloride are produced (Tilghmann, *Dingler's Jour.*, 1847, **106**, 196).

Siemens (*ibid.*, 1863, **169**, 207) reported that if water vapour is passed over a molten mixture of sodium chloride with twice its weight of calcium sulphate, hydrochloric acid, sulphur dioxide, and hydrogen sulphide are evolved, while a mixture of steam and carbon dioxide under the same conditions yields only sulphur dioxide and hydrochloric acid; the residue contained undecomposed sodium chloride, sodium hydroxide, calcium sulphide, calcium oxide, and small traces of sodium thiosulphate and sodium sulphide. It has been pointed out (Buff, *ibid.*, 1864, **172**, 282; Knapp, *ibid.*, 1872, **202**, 513) that in such reactions the materials of the containing vessel, *e.g.*, iron and silica, may play an important part, and the obvious incompatibility of some of the foregoing statements may well be due to such causes.

A recent investigation (Thompson and Tilling, *J. Soc. Chem. Ind.*, 1924, **43**, 39r) has shown that the ferrous sulphide formed, together with free sulphur, on heating pyrites in an inert atmosphere is decomposed (to form ferric oxide and hydrogen sulphide) at a lower temperature in steam than in carbon dioxide or air.

Thus it is evident that the previous investigations of the hydrolytic action of steam are few in number, and with the exception of the last cited, purely qualitative in kind. It has been the object of the present investigation to secure some numerical data in a few typical cases. A weighed quantity of the salt under investigation was heated to a known temperature for a definite time in a current of steam, and the issuing steam was condensed. Titration of this condensate with standard alkali gave a measure of the extent of hydrolytic decomposition which had occurred.

#### EXPERIMENTAL.

Steam was passed at a constant rate over a weighed quantity of material in a porcelain boat placed in a silica tube heated electrically to the desired temperature. In the hot zone, the silica was protected by a liner-tube of stout sheet nickel. Temperatures were measured by means of a platinum-platinum-rhodium thermo-

couple and a Paul millivoltmeter, the hot junction of the couple being held immediately above the boat containing the salt under investigation. The couple and millivoltmeter were standardised before and after use at 100° and at the melting points of tin, lead, zinc and sodium chloride, and found to give consistent readings trustworthy to about  $\pm 5^\circ$ .

Temperature readings were taken every ten minutes (or oftener) throughout the run, and at the end the condensed steam was titrated with *N*/10-sodium carbonate solution and methyl-orange, or, in the case of carbonates, by adding *N*/10-caustic soda solution and back-titrating with *N*/10-sulphuric acid, with phenolphthalein as indicator.

*Chlorides, Bromides, and Carbonates.*—The table gives the data relative to these salts.

Salt.	Weight (g.).	Temp.	Time (mins.).	Acid produced as c.c. of <i>N</i> /10- acid.	Wt. of salt decomposed in 30 mins. (calculated).
Calcium chloride .....	1.0	970°	30	99.53	0.553
" "	1.0	970	60	154.53	0.428
" "	0.5	812	60	65.5	0.182
" "	0.5	425	60	4.5	0.014
Strontium chloride ...	1.0	970	60	90.9	0.361
" "	0.5	812	60	6.5	0.026
" "	0.5	641	60	4.0	0.016
" "	0.5	638	60	0.5	0.002
Barium chloride .....	1.0	970	30	7.0	0.073
" "	1.0	970	60	19.1	0.099
" "	1.0	825	30	0.3	0.003
" "	0.5	809	60	Nil.	Nil.
Calcium bromide ...	0.5	690	30	31.6	0.316
" "	0.5	516	30	6.0	0.060
" "	0.5	463	30	4.8	0.048
" "	0.5	348	30	1.2	0.012
Strontium bromide ...	0.5	780	30	20.0	0.248
" "	0.5	575	30	6.2	0.076
" "	0.5	443	30	1.0	0.013
Barium bromide .....	0.5	770	30	5.0	0.075
" "	0.5	640	30	3.1	0.046
Calcium carbonate ...	1.0	558	45	13.7	0.046
" "	1.0	437	60	5.3	0.013
" "	1.0	390	60	Nil.	Nil.
Strontium carbonate.	1.0	679	60	9.5	0.035
" "	1.0	598	60	5.8	0.022
" "	1.0	455	60	0.3	0.001
Barium carbonate ...	1.0	980	60	38.6	0.190
" "	1.0	684	60	17.1	0.084

*Sulphates.*—At 970° the sulphates of calcium, strontium, and barium were not appreciably decomposed. From the first sample of barium sulphate used, a trace of sulphuric acid, equivalent to 1.2 c.c. of *N*/10-acid, was produced in the first 5 minutes. This was proved to be due to ferric sulphate present as an impurity.



The production of acid did not continue, there was no evidence of true hydrolytic action, and the residue was not alkaline.

*Phosphates.*—Calcium phosphate only was examined. This gave no evidence of hydrolytic decomposition even at 970°.

### Discussion.

The data recorded above make no claim to great precision, but the authors believe that they may properly be held to justify the following general conclusions.

The chlorides and bromides of calcium, strontium, and barium are all hydrolysed by steam under atmospheric pressure at high temperatures, the ease of decomposition decreasing with increasing atomic weight, the lowest temperature at which it is appreciable being as follows:

Calcium chloride . . .	425°	Calcium bromide . . .	348°
Strontium chloride . . .	640°	Strontium bromide . . .	443°
Barium chloride . . .	970°	*Barium bromide . . .	640°

\* Barium bromide appears to be appreciably volatile at 770°.

These figures afford some evidence that the bromides in general are more easily hydrolysed than the chlorides, and, in conjunction with the well-known difficulty of iodide preparation and the work of Fremy and Poulenc (*loc. cit.*) on the fluorides, show that the ease of decomposition for any alkaline-earth metal increases in the order fluoride, chloride, bromide, iodide, whilst for any particular halide it increases in the order barium, strontium, calcium.

In the case of the carbonates of strontium and barium the boat was obviously attacked and this renders the interpretation of the results doubtful. Calcium carbonate evidently decomposes appreciably at 440° in steam and it is interesting to compare this result with the previous observation (Pott, "Studien uber die Dissoziation von Calcium-Strontium- und Barium Karbonat," 1905) that measurable dissociation is observed at 525°.

Qualitative experiments with sodium and potassium nitrates showed that these were largely decomposed at temperatures just under 600°, leaving a strongly alkaline residue in the boat. The gaseous products comprised both nitric acid and oxides of nitrogen, but further investigation of this decomposition was abandoned, as it was likely to require an elaboration of experimental procedure disproportionate to the results anticipated.

The authors desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of them (H. C. S. to take part in this work.

CXVI.—*Studies with the Microbalance. Part III.*  
*The Filtration and Estimation of very small*  
*Amounts of Material.*

By ERNST JOHANNES HARTUNG.

QUANTITATIVE micro-analytical work involving precipitation and filtration is beset with considerable difficulty because errors due to adsorption, mechanical loss of material, solubility of precipitates, and accumulation of dust are apt to assume serious proportions in spite of the greatest care on the part of the operator. Moreover, the difficulty of estimating the magnitudes of these errors makes subsequent attempts to correct the experimental results very uncertain. In view of its importance, some preliminary work on the general analytical technique for dealing with 1—2 mg. of material was carried out in this laboratory in 1910 by G. A. Ampt, using the Steele-Grant microbalance. For filtering operations, he employed asbestos in small perforated silica crucibles weighing about 1 g. and transferred the precipitate into them in various ways. The results of his work (unpublished) showed that asbestos was unsuitable as a filtering medium for small amounts of material owing to mechanical and chemical alterations in weight, and that serious losses of precipitate were inevitable in any method of transference from one vessel to another. The obvious remedy is to carry out precipitation in the crucible itself and to adopt reversed filtration through a tube packed with platinum sponge for removal of mother-liquor and washings. Emich (*"Mikrochemisches Praktikum,"* 1924, p. 62) has described such a device for use with 5—10 mg. of material; asbestos is employed instead of platinum sponge and the precipitation vessel with its filtering tube (3—4 g.) is weighed on a Kuhlmann balance to the nearest 0.005 mg. A few examples of analyses are given in which the errors are quoted as usually below 1—2 parts per 1000. As far as the author is aware, however, no general methods for the accurate analysis of amounts of material weighing less than 1 mg. have hitherto been described. When, therefore, the need arose for estimating with precision the composition of very small quantities of mixtures of silver and silver iodide by a procedure involving filtration, the capabilities of the Steele-Grant microbalance were utilised in investigating the conditions for successful quantitative work. The original problem has not yet been solved satisfactorily owing to the great difficulty of separating completely silver iodide from silver, but the methods which have been developed are fairly general in application and may be of use to others who are con-

strained to work with very small amounts of material. The apparatus required consists of a sensitive microbalance (weighing to  $10^{-4}$  mg.), a silica crucible and filtering tube, a dust-free enclosure for carrying out filtration, an evaporator and electric oven, sundry small appliances such as silica pipettes, tubes, etc., and specially prepared reagents.

*The Microbalance.*—Two Steele-Grant instruments were available, each carrying a load of 100 mg. and weighing accurately to  $10^{-4}$  mg. It was impracticable to work with a crucible and filtering tube which weighed together less than 500 mg. and consequently one of the balances was modified to enable it to carry this load without material reduction in its absolute sensitiveness. In the usual form of the instrument, a constant weight fused to one end of the beam counterpoises a load hanging from a silica fibre attached to the other end. This load consists of a very light rack carrying the object to be weighed, certain small weights and a silica bulb by means of which the beam is equilibrated through alteration of air pressure in the balance case. The bulb constitutes the major portion of the load, since it must be stoutly blown in order to resist deformation with varying external pressure. By removing the bulb from the rack and fusing it to the other end of the beam as part of the constant weight, almost the whole of the load on the fibre is available for the object to be weighed. It is, of course, necessary to determine the displacement value of the bulb in its new position, since the ratio of the lengths of the balance arms now enters into each weighing, but this may easily be done by means of a small known weight, the value of which has been found against the bulb of an unmodified instrument in the usual manner. This procedure was followed with one of the two available balances, and weighings consistent to the nearest  $10^{-4}$  mg. could then be made in a load of 500 mg., or 1 part in  $5 \times 10^6$  parts. It is perhaps scarcely necessary to remark that, when material other than silica is weighed, certain corrections are required for the difference in density between silica and the material; but for quantities less than 1 mg., these may usually be neglected.

*Filtering Apparatus.*—The silica crucible in which the analytical operations are conducted is 5–6 mm. in diameter and about 16 mm. in depth (Fig. 1, E), with a capacity of 0.3 c.c. It is provided with two hooks for handling and suspension, the lower of which is shaped to act, in addition, as a support for the filtering tube during weighing so that the point of the tube does not rest on the bottom of the crucible. The tube (Fig. 1, F) is also made from vitreous silica, 30 mm. in total length and 0.3 mm. in bore. It is bent at a right angle in its upper portion and near the lower

end is a constriction above a 3—4 mm. column of platinum sponge. This is made by igniting ammonium chloroplatinate and introduced by suction in water, followed by careful compacting with a platinum wire. The lower orifice of the tube is then somewhat constricted in the oxy-gas flame. A suitable rate of passage of water through the finished filter with strong suction is about 3 c.c. per hour and finely-divided precipitates are completely retained by it. Care must be taken, however, that the filter is never ignited above a low red heat, otherwise the platinum sponge tends to shrink and

FIG. 1.

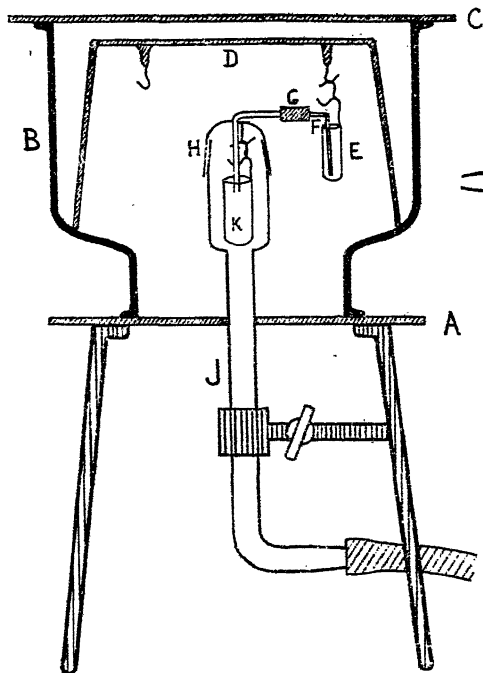
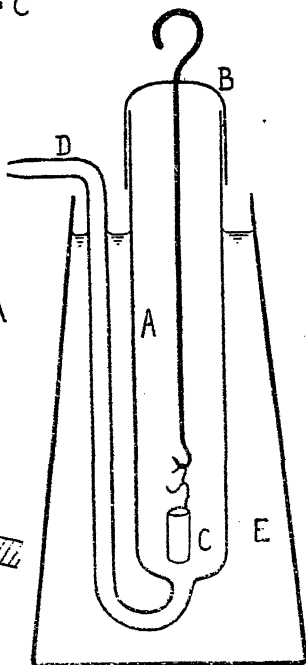


FIG. 2.



may leave channels which impair its filtering quality. Attempts were made to replace the platinum by finely-ground silica, firmly compacted and then sintered together, but shrinkage was so marked that the resulting filters were useless.

The dust-free enclosure in which filtration is carried out is shown in Fig. 1. A ground glass plate, A, with central perforation is cemented with pitch on top of an ordinary tripod with the ground surface upwards. On this rests a glass "dialysing jar" with ground ends, B, about 12 cm. in diameter and 10 cm. deep; this is closed above with the ground glass plate, C. On the ledge

inside the jar stands a light glass framework, D, provided with suitable hooks from one of which the crucible, E, hangs. The filtering tube, F, is inserted in a short length of clean rubber tubing, G, on the end of the arm of the ground cap, H, of a vertically clamped glass tube, J, which passes snugly through the central perforation of the base plate of the chamber. The enlarged upper end of this tube encloses a silica crucible, K, of rather more than 1 c.c. capacity, which hangs from a hook cemented to the inside of the ground cap. By this device, the filtrate from E may be collected in K without contamination or loss. The lower end of the tube J is connected to an exhaust pump or an evacuated receiver during filtration. The crucible E is introduced by means of a bent silica rod after raising C, and the filtering tube is inserted by a pair of narrow-pointed forceps into the moistened end of G after raising B. The tips of these forceps require special preparation; if they are made of smooth metal or ivory, there is great risk of the silica tube slipping out, whilst if the metal is roughened, some of it is gradually transferred to the smooth silica tube where it is visible as greyish weighable stains. This trouble was obviated by arming the tips with good quality calendered writing paper, cemented on with a little varnish and subsequently trimmed to shape with a razor. After placing the filtering tube and crucible in position, they are easily and safely adjusted for filtration by raising or lowering J and sliding B on A. No lubricant is used on any of the ground surfaces except that of the cap H and, if care be taken that none is allowed to soil the interior of the enlarged end of the tube J, the crucible K may be readily introduced or removed without fear of contamination. By means of this apparatus, distilled water and pure concentrated nitric acid may be passed repeatedly from the crucible through the filtering tube without changes in weight greater than 0.0001 mg. Such constancy is not possible, however, if crucible and tube are made of glass, owing to the solubility and hygroscopic character of this substance. For these reasons also, it is advisable to prevent contamination of the filtrate where this is undesirable, by making the ground cap H and its arm from vitreous silica.

*Evaporator and Electric Oven.*—An evaporator is necessary in which liquids may be evaporated, or kept hot in order to coagulate precipitates, with complete protection from dust. A simple and efficient form is shown in Fig. 2; the wide glass tube, A, is 3.5 cm. in diameter and 18 cm. long and is closed above by a loosely fitting cap, B, carrying a vertical glass rod with a hook from which the crucible, C, hangs. The lower portion is immersed in a glycerol bath, E, regulated in temperature by hand, and a stream of pure

dry filtered air is passed continuously through the tube D. In this way, exclusion of dust is assured and, if the glycerol be kept at 130—150°, aqueous solutions may be rapidly evaporated in a few minutes without loss by boiling or spraying. A small electric oven is used for ignitions up to a dull red heat; it consists of a vertical silica tube sealed at the lower end and surrounded with the usual heating coils and packing. The lid is a silica watch-glass, to the convex lower side of which is sealed a silica hook for suspending the objects to be heated. This cover is provided with a small silica handle and the upper part of the oven is covered with an inverted glass basin as a protection from dust.

*Reagents.*—Special purification of all reagents was found to be necessary, particularly as regards freedom from dust. Water was twice distilled in a silica apparatus in the usual way and preserved in a capped silica flask. The residue on evaporation corresponded to 1 mg. per litre, which included any dust contamination during the operation and was insignificant as a source of error. Acids, ammonia, and other liquids were distilled immediately before use by heating them in conical flasks and exposing to the vapours the outside of a clean silica test-tube full of water. The condensed drops were removed by an ignited silica pipette, fashioned like a medicine dropper, and either added at once to the crucible, or diluted to the required degree with water in small, covered silica tubes. Solid reagents were obtained by twice crystallising the best commercial analytical reagents in silica vessels, special care being taken to avoid contamination with fibres and dust.

The general technique for carrying out an analysis is as follows: The crucible and tube are cleaned by boiling concentrated nitric acid, washed repeatedly with water, dried over a small alcohol flame, and weighed together. During these operations, the crucible is handled on the end of a silica rod and, when clean, hangs from a silica hook mounted on a cork and protected from dust by a glass cover. After weighing, the filtering tube is removed from the crucible by forceps, the sample introduced, the tube replaced in its support so that the lower end does not come in contact with the sample, and the whole reweighed. The filtering tube is then put in place in the filtering apparatus, and the material in the crucible is dissolved by introduction of one or two drops of the appropriate solvent by a silica pipette, followed by heating, if necessary, in the evaporator. It has been found that even if effervescence takes place during solution, *e.g.*, calc-spar in acid, no loss by spraying occurs owing to the depth of the crucible and the very small amount of gas evolved. The precipitating agent is then added and the crucible is heated in the evaporator until

clotting of the precipitate, or sufficient increase in grain size, has taken place. The crucible is then cooled in the filtering chamber, the liquid removed by the filtering tube, and the precipitate washed. The only satisfactory criterion of complete washing is the constancy in weight of the residue, but three or four applications of a few drops of the washing liquid are usually ample, since the filtering tube removes the liquid completely. Should the tube become choked, making filtration very slow, it may be freed by detaching the vertical tube, J (Fig. 1), from the exhaust pump and blowing into it for a few moments. When washing is finished, the filtering tube is detached from the rubber and placed in its support in the crucible, after its upper end has been rinsed with a drop or two of water. The whole is then dried in the evaporator, ignited, if necessary, and finally weighed. Analogous methods may also be applied to the filtrate in the crucible K (Fig. 1), should further analysis of this be desired.

In order to test the general accuracy attainable with this apparatus, certain standard analyses were performed after the various inherent sources of error in each case had been discovered and guarded against. The results are summarised in Table I, in which

TABLE I.

*Estimation of positive radicals in pure salts.*

Expt.	Salt.	Weight in mg.	Estimated as	Weight of ppt. in mg.	% of positive radical.	Pure salt requires
1	AgNO <sub>3</sub>	0.6833	AgCl	0.5763	63.47	63.50
2	"	0.3994	"	0.3355	63.22	
3*	"	0.1877	"	0.1548	62.1	
4	KCl	0.8895	KClO <sub>4</sub>	1.6455	52.20	52.44
5	"	0.7829	"	1.4529	52.37	
6	"	0.0965	"	0.1808	52.9	
7	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.9024	PbSO <sub>4</sub>	0.8242	62.38	62.55
8*	"	0.8245	"	0.7498	62.11	
9	"	0.1649	"	0.1503	62.25	
10	BaCl <sub>2</sub>	0.9288	BaSO <sub>4</sub>	1.0309	65.33	65.94
11	"	0.2856	"	0.3173	65.40	
12	CaCO <sub>3</sub>	0.4469	CaC <sub>2</sub> O <sub>4</sub>	0.5767	40.38	40.04
13	"	0.3510	"	0.4471	39.86	
14	"	0.1482	CaCO <sub>3</sub>	0.1474	39.8	
15	"	0.0878	CaSO <sub>4</sub>	0.1209	40.5	
16	"	0.0844	"	0.1161	40.5	

\* Known source of error.

all weights are given in milligrams; they have not been specially selected and are therefore typical of the methods described. Carefully purified and tested salts were used, and the positive radicals were estimated in each case. Inspection of the figures shows that

the analyses are reasonably accurate even for quantities of material as small as 0.1 mg., where the errors in the examples tried have not exceeded 1%, and for larger amounts the errors are usually much less proportionately.

There are several sources of error which, though easily controlled in ordinary routine, are apt to assume serious proportions in micro-analytical work of this kind. The most variable of these is due to accumulation of dust, particularly when the crucible and tube are wet; however, a number of trials has shown that, by reducing to a minimum the time during which the apparatus and reagents are freely exposed, by avoiding agitation of liquid reagents, and by washing down the outside of the pipette with a few drops of water immediately before introducing any liquid into the crucible, errors due to dust are insignificant except when dealing with less than 0.1 mg. of material. Mechanical loss of precipitate is another source of error which has caused some trouble, especially when dealing with very finely-divided precipitates which cannot be made coarse-grained by the usual analytical methods. For example, it is practically impossible to precipitate at boiling temperature without loss in a small crucible with 2 or 3 drops of solution, and the only remedy is fairly prolonged heating after precipitation until the solid settles readily. Further, when washing such a precipitate as calcium oxalate, it is essential to allow the drops of washing liquid to fall into the crucible without forming a bridge between this and the point of the pipette, otherwise some of the solid will spread on the latter and be lost. Errors due to adsorption are also difficult to control and are generally much more serious than in ordinary analytical work, for a fraction of a drop may mean a large excess of reagent. For example, calcium oxalate precipitated with a considerable excess of ammonium oxalate may contain as much as 10% of its weight of the ammonium salt, which cannot be removed by washing; in this case, careful ignition of the precipitate to the carbonate at 400° removes the difficulty completely, but the general remedy is to use dilute solutions of reagents of known concentration. When adsorption cannot be prevented, it is sometimes possible to wash out the adsorbed material after ignition of the precipitate, as with barium chloride on barium sulphate (Pregl, "Organische Mikroanalyse," 1923, p. 147), or to estimate it by some means, as with silver nitrate or silver iodide by evaporation with a drop of dilute hydrochloric acid. The most serious of all sources of error is, however, the solubility of the precipitate, especially in the washing liquid. The reason is that the amount of liquid necessary is out of all proportion to the amount of precipitate, because it is mainly used in washing the interior of



the crucible. It is rarely possible to employ less than 0.5 c.c., which, for 0.5 mg. of precipitate, corresponds to 1 litre per g. and involves a possible error of 1%, if the solubility of the precipitate is 10 mg. per litre. In Table I, Experiment 3 shows the effect of using too great an excess of hydrochloric acid in precipitating silver chloride, owing to increased solubility of the salt. Expt. 8 shows the effect of washing with dilute sulphuric acid, in which lead sulphate has the minimum solubility of 5 mg. per litre, instead of diminishing the solubility still further by addition of alcohol, as in Expts. 7 and 9. Some error due to solubility is inevitable, but it may be diminished by careful regulation of the conditions of precipitation, proper choice of the washing liquid, and strict economy in its use. It is, of course, possible to employ a saturated solution of the precipitate itself for washing, but great care is necessary to avoid introduction of solid particles. This procedure has not been adopted in obtaining the results given in Table I, nor have corrections for any possible sources of error been applied.

The technique described may easily be extended to a large number of micro-analytical problems, provided that these are not too complex. There is, of course, no point in using the micro-balance for analysis when sufficient material for the usual laboratory procedure is available, although in some cases, the instrument offers a more accurate and much more expeditious method. For example, the composition of a mixture of sodium and potassium chlorides may be determined rapidly and accurately by evaporating less than 0.5 mg. with a single drop of nitric acid and weighing the mixed nitrates in the residue. Apart, however, from the fact that the chance of accidental error is always greater when dealing with very small quantities, the application of the Steele-Grant micro-balance to analytical problems has certain limitations. Volatile liquids cannot be weighed without much trouble, although, when the composition of a liquid is in question, it may be measured with a small pipette. The simplest way to calibrate a pipette for use with the microbalance is to make up an aqueous solution of some stable anhydrous salt (*e.g.*, potassium chloride) of known concentration in the usual manner; a pipette-full of this solution is then evaporated to dryness and the residue weighed on the micro-balance. Volatile solids and hydrated salts cannot usually be weighed without special contrivances, and also correct sampling of small amounts of heterogeneous material is extremely difficult. Further, some gelatinous precipitates are awkward to manipulate with the filtering tube owing to the tendency to become impacted in the end of it. Nevertheless, in spite of these limitations, the apparatus and micro-analytical methods here described have a

considerable range of application with accuracy, and it is hoped that they may be of use to other investigators who find it necessary to work with very small amounts of material.

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## CXVII.—*The Ternary System Sodium Thiosulphate-Sodium Sulphate-Water.*

By RICHARD RANDOLPH GARRAN.

THE system sodium thiosulphate-sodium sulphate-water has been examined at 0.8°, 18°, 25° and 40°, the temperature being maintained constant to within 0.02° in the last three cases and to within 0.1° in the first. The transition between decahydrated and anhydrous sodium sulphate in presence of sodium thiosulphate has also been studied.

Mixtures, prepared as indicated in the descriptions of the various isotherms, were rotated in stoppered glass tubes in a thermostat for periods varying from 3 to 24 hours; then, after allowing the solid to settle, a definite volume of solution was drawn off by means of a pipette fitted with a cotton-wool filter and weighed in a tared bottle; the solid was rapidly drained on a Büchner funnel and a portion of it weighed. The solution was diluted and the solid dissolved to known volumes in each case and aliquot parts of these were taken for analysis. The values of the densities of the solutions are probably not accurate beyond two or three units in the third decimal place.

Thiosulphate was determined by adding a known small excess of standard iodine solution and titrating this excess with a solution of sodium thiosulphate the normality of which was obtained from a hydrochloric acid solution (standardised against calc-spar) by means of a mixture of potassium iodide and iodate.

For the determination of the sulphate, the following methods were decided upon after many trials:

(i) The solution was evaporated to dryness with excess of sulphuric acid, and the residue heated to convert it completely into sulphate and to drive off the excess of acid and the sulphur which was formed. From the total weight of sulphate present and the known amount of thiosulphate, the amount of sulphate originally present was readily calculated.

(ii) The solution of thiosulphate was oxidised, by heating with bromine water in the presence of a little alkali, in accordance with the following equation (Mayr and Peyfuss, *Z. anorg. Chem.*, 1923,

127, 123; 1924, 131, 203):  $\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Br}_2 + 5\text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + 8\text{HBr}$ . After the excess of bromine had been expelled, the sulphate was precipitated as barium sulphate and the amount of sodium sulphate originally present calculated as above.

(iii) When thiosulphate was present in large excess, method (ii) was found to be untrustworthy. The sulphate present was then precipitated as barium sulphate in cold neutral solution (barium thiosulphate is soluble under these conditions), allowed to settle for 24 hours, and washed three times by decantation, being allowed to settle during 18 to 24 hours each time. The precipitate was then boiled with dilute hydrochloric acid to make it coarser, filtered off, and weighed. This method was found to be trustworthy, but the time required was considerable.

The isotherms at  $0.8^\circ$  and  $25^\circ$  are based entirely on analyses by the first method: that at  $18^\circ$  almost entirely, and that at  $40^\circ$  partly, on the second and third methods. Compositions are expressed as percentages of components by weight, and mixed crystals are indicated in the tables by *M.C.* followed by the formula of the major constituent.

### *Discussion of Results.*

The results obtained at  $0.8^\circ$  and  $18^\circ$  are shown in Tables I and II and are plotted in the usual triangular diagram in Fig. 1. Only the solution curves at  $0.8^\circ$  are shown, as the two systems are of similar general form. Suitable mixtures were prepared from water, pure (A.R.) crystals of sodium thiosulphate pentahydrate and pure commercial (B.D.H.) crystals of sodium sulphate decahydrate, and heated to homogeneity in stoppered tubes which were then rotated in a thermostat for several hours (generally over-night) after the solid had settled out. In a few cases, in solutions containing a preponderance of thiosulphate, it was necessary to seed the mixture in order to induce crystallisation.

In Fig. 1 the curve *ab* denotes solutions in equilibrium with solids along the line *a'b'*, which is so short that it gives only very slight evidence of mixed-crystal formation between  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and (possibly)  $\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ . The curve *bc* denotes solutions in equilibrium with solids along the line *b''c'*, and here there is definite evidence of mixed-crystal formation between decahydrates. The extent of this at  $0.8^\circ$  and  $18^\circ$  is approximately the same.

The two-phase dried solids along the line *b'b''*, which are in equilibrium with the solution at the condensed triple point *b*, were obtained by prolonged drying of the moist solid on blotting paper in a desiccator over the solution *b* at the temperature of the isotherm. Washing with alcohol resulted in partial dehydration of the crystals.

TABLE I.  
Isotherm at 0.8°.

Solutions.			Wet solids.		Solid phases.
Density.	% Na <sub>2</sub> SO <sub>4</sub> .	% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	% Na <sub>2</sub> SO <sub>4</sub> .	% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	
1.040	4.60	0.00	—	—	Na <sub>2</sub> SO <sub>4</sub> , 10H <sub>2</sub> O.
1.065	3.13	4.48	36.30	1.08	M.C. Na <sub>2</sub> SO <sub>4</sub> , 10H <sub>2</sub> O.
1.105	2.31	9.63	35.48	2.25	
1.159	1.88	16.03	31.91	4.95	
1.190	1.87	19.62	34.68	5.41	
1.247	1.56	25.63	32.14	9.38	
—	1.34	30.07	30.10	10.39	*
1.312	1.27	32.26	32.84	9.28	
1.324	1.58	33.91	29.10	12.47	
—	—	—	32.80	14.86	M.C. Na <sub>2</sub> SO <sub>4</sub> , 10H <sub>2</sub> O and M.C. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.
1.314	1.22	32.72	15.49	36.80	
—	—	—	15.83	39.67	
—	—	—	12.82	44.51	M.C. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.
1.317	1.15	32.77	9.10	45.07	
1.317	1.44	32.72	0.56	61.12	
1.315	—	33.57	—	—	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.

\* Metastable.

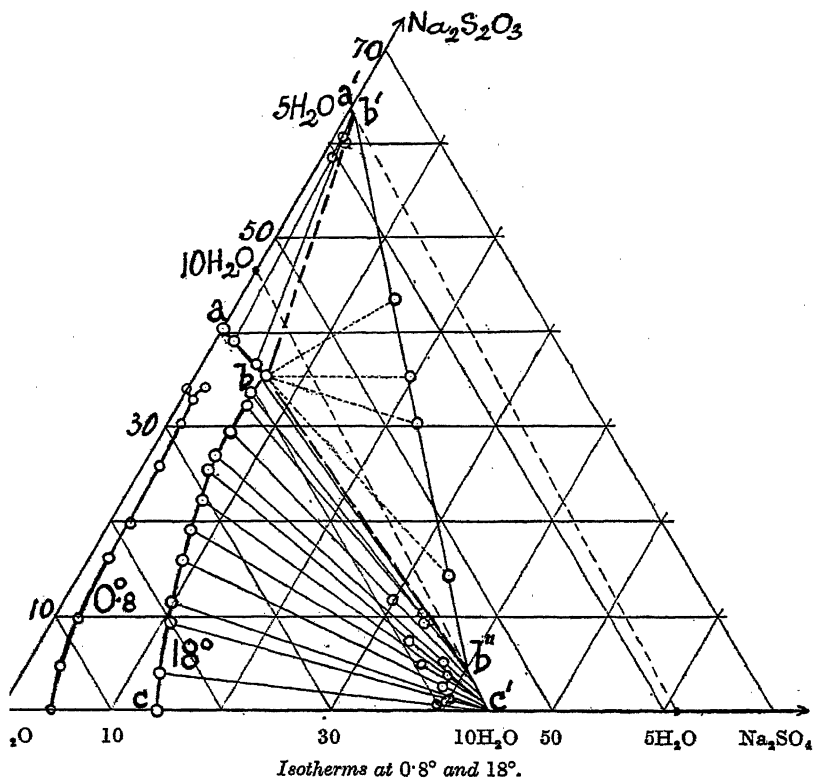
TABLE II.  
Isotherm at 18°.

Solutions			Wet solids.		Solid phases.
Density.	% Na <sub>2</sub> SO <sub>4</sub> .	% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	% Na <sub>2</sub> SO <sub>4</sub> .	% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> .	
1.130	14.11	—	—	—	Na <sub>2</sub> SO <sub>4</sub> , 10H <sub>2</sub> O.
1.150	12.31	4.01	39.21	0.75	M.C. Na <sub>2</sub> SO <sub>4</sub> , 10H <sub>2</sub> O
1.180	10.71	9.36	40.14	1.21	
1.194	9.83	11.34	37.22	2.75	
1.225	8.45	15.86	38.75	2.52	
1.248	7.65	19.16	35.84	4.75	
1.276	7.14	22.46	38.64	3.60	
1.301	6.01	25.53	33.34	7.45	
1.314	5.97	27.00	37.59	5.11	
1.338	6.04	29.57	29.66	11.65	
1.356	6.32	32.31	33.92	9.18	
1.374	5.94	33.66	33.20	10.14	M.C. Na <sub>2</sub> SO <sub>4</sub> , 10H <sub>2</sub> O and M.C. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.
1.390	6.14	35.07	34.12	9.63	
1.399	6.26	35.42	33.40	14.30	
—	—	—	22.64	30.40	M.C. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.
—	—	—	19.40	35.46	
—	—	—	13.99	43.59	
1.394	6.31	35.46	1.02	60.02	M.C. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.
1.395	4.87	36.61	0.79	60.73	
1.384	1.65	39.12	0.65	58.54	
1.378	—	40.36	—	—	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 5H <sub>2</sub> O.

The positions of these solids in the diagram along the line joining the end members, *b'* and *b''*, of the two series of mixed crystals provide strong evidence for the existence of the two series.

The isotherm at  $40^\circ$  (see Table III and Fig. 2) also consists of two curves,  $ad$  denoting solutions in equilibrium with solids along the line  $a'd'$ , and  $df$  solutions in equilibrium with solids along the line  $d''f'$ . Again the larger range is that of mixed crystals at the sulphate end, but at this temperature between anhydrous salts, whilst that showing mixed-crystal formation between  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

FIG. 1.

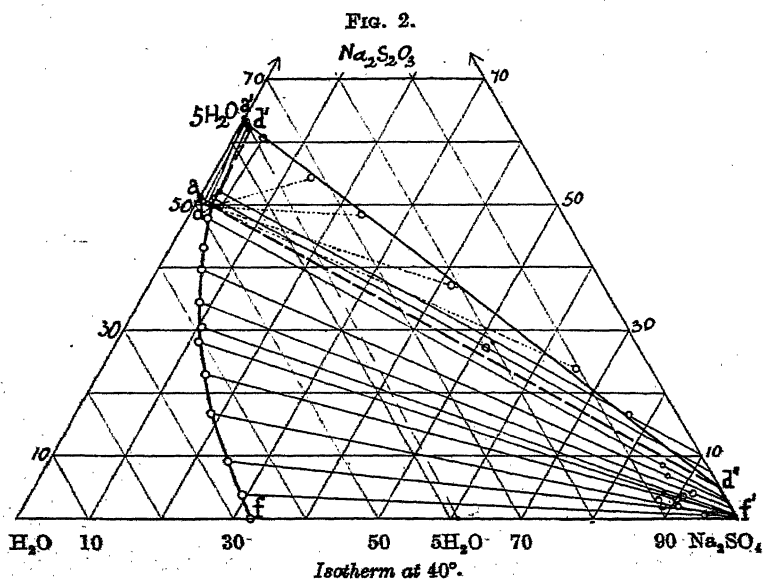


and (presumably)  $\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , although more extensive than at lower temperatures, is still very small. The dried solids along the line  $d'd''$  were obtained by washing the moist solid with warm methylated spirit and drying carefully between folded blotting paper. It was found very difficult in this case to remove all moisture from the solid owing to the finely-divided nature of the anhydrous sodium sulphate which was formed. The complexes in this isotherm were prepared by evaporation, under diminished

TABLE III.  
Isotherm at 40°.

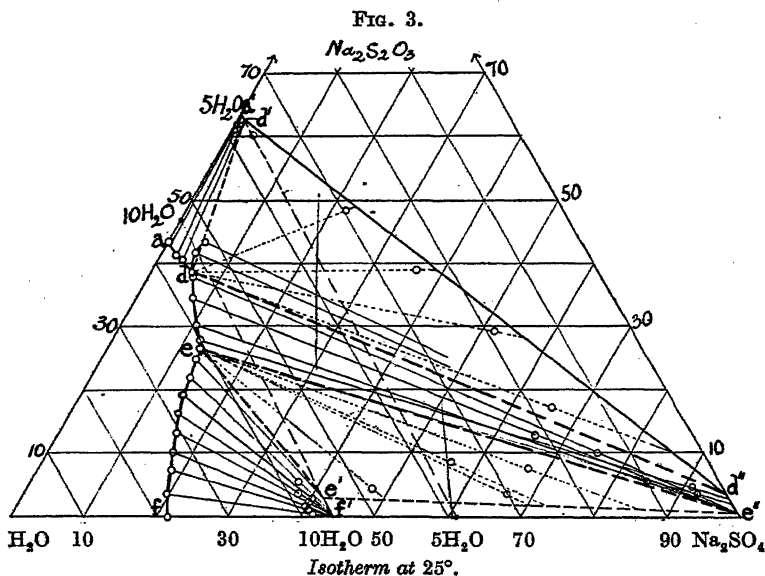
Solutions.			Wet solids.		Solid phases.
Density.	% $\text{Na}_2\text{SO}_4$ .	% $\text{Na}_2\text{S}_2\text{O}_3$ .	% $\text{Na}_2\text{SO}_4$ .	% $\text{Na}_2\text{S}_2\text{O}_3$ .	
—	32.37	—	—	—	$\text{Na}_2\text{SO}_4$ .
—	29.35	3.79	95.25	0.37	}
1.326	24.79	9.06	96.23	0.84	
1.334	18.58	16.73	90.67	1.84	
—	14.76	22.95	90.50	2.87	
1.367	11.14	28.06	87.65	3.98	
—	10.40	30.44	90.85	3.29	}
1.383	8.13	34.35	91.85	3.93	
—	5.90	39.74	86.98	6.80	
1.444	4.28	43.06	81.30	8.81	
1.484	2.46	48.78	85.56	8.29	
—	1.79	51.04	51.47	27.10	*
—	2.03	52.10	76.77	16.38	*
—	—	—	95.33	2.87	}
1.496	2.27	49.38	65.72	23.80	
1.496	2.08	49.72	41.80	37.03	
1.494	2.24	49.73	23.68	48.26	
—	2.09	49.97	13.82	54.14	
—	3.61	49.60	4.06	60.68	}
1.493	2.14	49.88	1.51	62.00	
—	2.45	49.98	0.28	63.41	
—	1.58	50.15	0.00	63.26	
1.492	0.67	50.49	0.00	64.58	
1.488	—	51.23	—	—	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .

\* Metastable.



pressure, of solutions unsaturated at  $40^\circ$ , using the method employed by Rivett and Lewis (J., 1924, 125, 1163).

The transition point between decahydrated and anhydrous sodium sulphate will be depressed by the addition of sodium thiosulphate to the solution. With an appropriate mixture in a Dewar flask fitted with thermometer and stirrer, temperature-time curves on heating and cooling were obtained. The mixture was heated at  $70^\circ$  for an hour to hasten the formation of mixed crystals and then cooled to  $15^\circ$ , being well inoculated with crystals of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . On slow re-heating, this gave



a well-defined arrest at  $20\text{--}30^\circ$  and on cooling at  $19\text{--}80^\circ$ . These temperatures were accurately reproducible, both with the same and with fresh mixtures. The cooling curve was of the usual form, showing undercooling followed by a rise in temperature to the arrest point on seeding. Samples of the solutions in equilibrium with the three solid phases at the arrest points, both on heating and on cooling, were drawn off and analysed, the mean composition being 7.95% of sodium sulphate and 35.0% of thiosulphate. The difference between the two temperatures is probably accounted for by the slow rate of diffusion in the solid phases, the mixed crystals forming above and below the quadruple point being of slightly different compositions. The true transition point should lie between these two temperatures, at about  $20\text{--}05^\circ$ .

TABLE IV.  
Isotherm at 25°.

Solutions.			Wet solids.		Solid phases.
Density.	% $\text{Na}_2\text{SO}_4$ .	% $\text{Na}_2\text{S}_2\text{O}_3$ .	% $\text{Na}_2\text{SO}_4$ .	% $\text{Na}_2\text{S}_2\text{O}_3$ .	
1.204	21.60	—	—	—	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.215	19.74	3.48	41.43	0.34	
1.236	18.44	7.30	40.30	1.06	
1.253	17.12	10.14	39.79	1.56	M.C. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.271	16.13	13.22	39.83	2.23	
1.288	14.86	16.16	37.80	3.50	
1.311	13.97	19.35	40.07	2.94	
—	13.62	22.02	36.85	5.51	
1.359	12.97	24.96	—	—	M.C. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and M.C. $\text{Na}_2\text{SO}_4$ .
—	—	—	47.50	4.44	
—	—	—	66.38	3.60	
—	12.72	26.86	56.17	8.65	M.C. $\text{Na}_2\text{SO}_4$ .
—	12.72	26.65	67.08	7.77	
—	13.27	26.12	92.50	3.53	*
1.379	12.15	28.00	91.15	4.70	
—	10.28	30.31	84.66	5.52	M.C. $\text{Na}_2\text{SO}_4$ .
1.401	7.73	34.72	65.45	12.94	
—	6.06	38.07	75.62	10.08	
—	4.53	41.86	—	—	*
1.453	4.87	43.32	—	—	
—	5.59	38.83	65.72	17.16	M.C. $\text{Na}_2\text{SO}_4$ and M.C. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .
—	5.66	38.67	51.92	29.11	
1.426	5.64	38.97	36.12	38.99	
1.420	5.42	38.85	21.86	48.30	M.C. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .
—	5.20	38.96	3.36	60.33	
1.418	4.69	39.45	0.92	61.97	
1.412	3.13	40.92	0.00	63.46	
1.411	2.01	41.53	0.51	61.14	
1.410	0.23	43.52	0.22	62.32	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .
—	—	43.50	(from tables)	—	

\* Metastable.

The isotherm at 25° should then show three curves, since three solid phases may exist at this temperature. The results obtained are in Table IV and are plotted in Fig. 3. The isotherm consists of three curves: *ad* denoting solutions in equilibrium with mixed crystals along the small range *a'd'* (mainly  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), *de* denoting those in equilibrium with mixed crystals along the line *d''e''* (mainly anhydrous  $\text{Na}_2\text{SO}_4$ ), and *ef*, where the equilibrium is with mixed crystals along *e'f'* (mainly  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). The solids along *e''e'* were dried on blotting paper and those along *d'd''* were washed with spirit.

The existence of mixed crystals of decahydrates of the two salts and of a very small range of pentahydrates is clearly shown. The evidence obtained here for the series of mixed crystals of anhydrous salts is not definite, but the work at 40° points to the existence of an analogous series at 25°. The solutions in this isotherm were prepared by dissolving the salt constituent which should mainly



constitute the solid phase in the total amount of water required, then adding the other salt, and rotating the tube in the bath.

The sodium sulphate solution curve has been extended into the metastable region at  $0.8^\circ$ ,  $25^\circ$  and  $40^\circ$ , and in each case it shows a decided increase in curvature. If the metastable solution curve in a system where mixed crystals are formed could be fully realised, it should form a closed loop, and this is indicated by the shapes of the curves in the metastable region.

### *Summary.*

1. The system sodium thiosulphate-sulphate-water has been examined at  $0.8^\circ$ ,  $18^\circ$ ,  $25^\circ$ , and  $40^\circ$ .

2. The existence has been demonstrated of a very short series of mixed crystals of pentahydrates at all four temperatures; of a series of decahydrates at  $0.8^\circ$ ,  $18^\circ$ , and  $25^\circ$ ; and of a series of anhydrous salts at  $25^\circ$  and  $40^\circ$ .

3. The quadruple point at which four phases co-exist, three being mixed crystals and one a solution, is at a temperature very close to  $20^\circ$ .

The author is indebted to Professor A. C. D. Rivett for suggesting this work and for advice during its progress.

UNIVERSITY OF MELBOURNE.

[Received, February 9th, 1926.]

## CXVIII.—*The Ternary System Sodium Sulphide-Sodium Sulphate-Water.*

By ARTHUR ROBERT HOGG.

THE fact that anhydrous sodium sulphite and sulphate, and their corresponding hydrates, crystallise together within limits (Rivett and Lewis, *Rec. trav. chim.*, 1923, 42, 954; J., 1924, 125, 1156, 1162) suggested an inquiry into the relations between sodium sulphide and sodium sulphate. This has been carried out at each of the five temperatures  $0.1^\circ$ ,  $18^\circ$ ,  $25^\circ$ ,  $31^\circ$  and  $40^\circ$ , the complete ternary system being described in each case.

For the most part the salts used have been of analytical reagent (B.D.H.) standard. Mixtures of these and water in varying amounts have been brought to equilibrium in rubber-stoppered glass tubes, the proportions taken being such that about 6% of the total was present as solid when equilibrium was attained. Three methods of attaining equilibrium were employed: (i) cooling homogeneous solutions from higher temperatures, inoculating, if necessary, with

the appropriate solid phase (systems at  $0.1^{\circ}$  and  $18^{\circ}$ ): (ii) heating heterogeneous mixtures from lower temperatures (systems at  $25^{\circ}$  and  $31^{\circ}$ ): (iii) evaporating homogeneous solutions under reduced pressure at the temperature of experiment until sufficient solid appeared (system at  $40^{\circ}$ ). When all phases were present, the tubes were mechanically rotated in a thermostat for from 4 to 40 hours.

The second method is satisfactory in giving the course only of the solution curves: it will not give accurate information as to compositions of solid phases, but it sufficed in the cases where it was used. The third method was carried out in tubes fitted with vertical side limbs and connected in batches of six with a small cooled receiver exhausted to about 40 mm. pressure. The tubes were clamped horizontally to a tilting platform in the bath and were gently rocked during the evaporation, which generally occupied about 3 hours. In order to avoid possible loss of hydrogen sulphide, the mixtures were kept in connexion with the pump for as short a time as possible, the vacuum being maintained by condensation. The distillate from six tubes was collected and tested for sulphide. The amount found, part of which was due to priming, was insufficient to affect the analyses appreciably. When sufficient solid had separated, the vacuum was broken and the rocking continued for from 2 to 12 hours.

On attainment of equilibrium, a sample of the solution was withdrawn in a pipette (suitably heated or cooled) through a cotton-wool plug, and weighed. Densities so obtained are correct to one or two units in the third decimal place. Dilution to an appropriate extent gave the solution which was analysed. The moist solid was obtained by rapid filtration on a Büchner funnel and a weighed amount was dissolved to a known volume. In some cases, the wet solid was washed with alcohol and dried between folds of blotting paper. In analysis, sulphide was determined by titration against standard acid, with phenolphthalein as indicator, and sulphate was determined gravimetrically as barium sulphate.

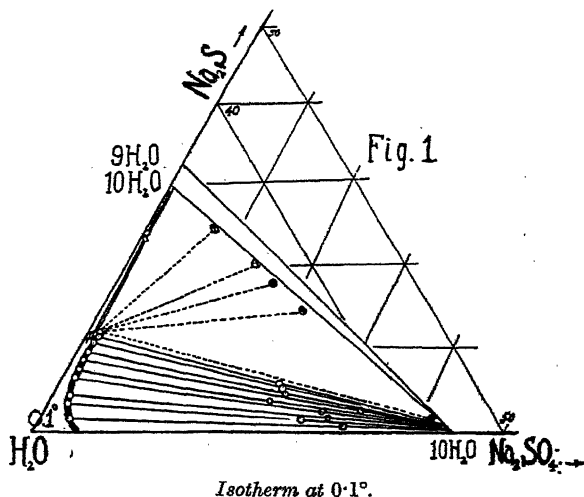
#### *Discussion of Results.*

The experimental results are given in Tables I to VI. Compositions are expressed in % of anhydrous salt by weight. In the last column, mixed crystals are indicated by M.C. followed by the formula of the major constituent.

The first point to be noted is that at  $0^{\circ}$  sodium sulphide has been obtained as a decahydrate, a form apparently not hitherto described. Analysis of the solid, after washing with alcohol and drying with blotting paper, gave  $\text{Na}_2\text{S}$ , 30.04% :  $\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O}$  requires 30.23 and  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  requires 32.49%. In the ternary system at  $0.1^{\circ}$  the

TABLE I.  
Isotherm at 0.1°.

Solutions.			Wet solids.		Solid phases.
$D_4^{\circ}$ .	% by weight. $\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	% by weight. $\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	
1.122	11.33	—	30.0	—	M.C. $\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O}$ .
1.125	11.34	0.63	23.4	0.12	
—	11.22	0.93	23.1	0.43	
1.137	11.94	1.16	—	—	M.C. $\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O}$ and M.C. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.131	11.21	1.23	29.6	0.96	
1.130	11.14	1.25	25.1	7.30	
1.131	11.23	1.19	21.1	13.54	
1.129	11.16	1.16	18.49	16.53	
1.129	11.18	1.23	18.34	16.53	
1.132	11.23	1.18	14.49	21.0	
1.129	11.11	1.19	0.47	43.2	M.C. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.124	10.77	1.24	5.56	23.6	
1.110	9.49	1.27	4.49	24.2	
1.099	8.32	1.28	2.59	33.5	
1.091	7.36	1.48	3.60	23.6	
1.081	6.16	1.54	2.48	28.9	
1.066	4.79	1.68	1.64	30.6	
1.052	3.16	2.11	1.49	27.5	
1.041	1.44	2.99	0.45	32.5	



solution curve for this decahydrate is short (see Fig. 1), but there is definite indication of the separation of mixed crystals containing a very little  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

At the sodium sulphate end the mixed-crystal formation is greater, the limiting member of the series containing 42% of sulphate and 1.5% of sulphide. The points in Fig. 1 marked by crosses within

FF\*

circles represent mixtures of two solid phases in equilibrium with the solution at the intersection of the two solution curves. The solids were obtained almost free from mother-liquor by washing with alcohol and drying with blotting paper. It will be seen that they all lie very near to the line joining the end corresponding to mixed crystals of (mainly)  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  containing sulphide and the point representing the composition  $\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O}$ . This gives independent proof of the existence of a decahydrate of the sulphide.

Between it and the nonahydrate in the binary system the transition point has been shown by the cooling method to be  $4.7^\circ$ , the saturated solution then containing 12.46% of sodium sulphide and having a density of 1.128.

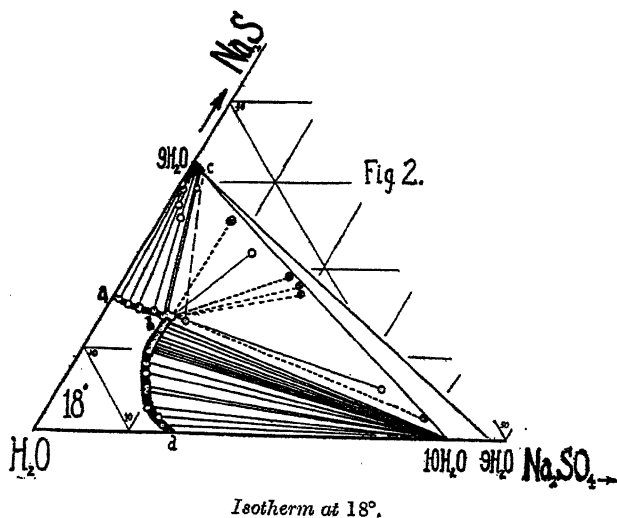
TABLE II.  
Isotherm at  $18^\circ$ .

Solutions.			Wet solids.		Solid phases.
$D_4^{20}$ .	% by weight. $\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	% by weight. $\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	
1.169	15.95	—	—	—	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .
—	15.65	0.53	30.40	0.32	
—	15.33	2.28	29.27	0.63	
1.187	15.08	3.47	28.15	1.11	
1.197	14.50	5.20	25.96	2.13	M.C. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .
1.212	14.02	5.83	31.56	0.74	
—	13.98	6.44	30.10	1.66	
—	—	—	25.56	7.61	
1.212	13.90	7.21	22.23	11.91	M.C. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
—	—	—	19.31	17.54	
1.210	13.95	7.24	18.38	18.91	
—	—	—	16.93	19.49	
1.205	13.84	7.22	5.12	33.99	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.210	13.98	7.23	2.56	40.28	
—	13.78	7.16	0.65	42.91	
1.225	13.15	9.75	31.50	1.75	
1.208	13.08	7.01	4.12	32.11	
1.195	12.46	7.00	2.93	35.21	
1.186	12.14	6.93	3.62	32.98	
1.180	11.16	6.79	—	—	
1.175	10.91	6.96	2.08	37.68	
1.169	10.33	7.19	2.35	35.61	
1.167	10.04	7.17	3.13	32.89	
1.165	9.96	7.09	1.04	40.70	
1.162	9.47	7.15	2.20	35.82	
1.149	7.99	7.64	1.82	35.84	
1.143	6.82	8.09	1.88	33.39	
1.132	5.33	9.05	1.32	34.65	
1.130	4.54	9.30	0.93	36.79	
1.131	2.84	10.67	0.54	37.27	
1.126	1.51	11.91	0.37	36.05	
1.126	0.62	13.31	0.15	36.17	

At  $18^\circ$  (Table II) the solid separating at the sulphide end is the ordinary nonahydrate containing some dissolved sulphate (see

Fig. 2). Whether the latter is there with water in the same molecular proportion of 1 : 9 cannot be stated. At the sulphate end, however, there is no indication of any appreciable solubility of sodium sulphide in  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . It would seem that  $\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O}$  cannot exist in mixed crystals at  $18^\circ$ , while the nonahydrate of the sulphide is insoluble in the decahydrate of the sulphate.

There is no appreciable mixed-crystal formation at  $25^\circ$  or  $31^\circ$  (Tables III and IV) either in the hydrated or anhydrous sulphate



*Isotherm at  $18^\circ$ .*

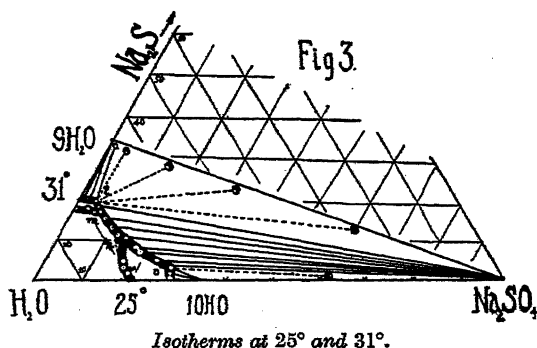
TABLE III.

*Isotherm at  $25^\circ$ .*

Solutions.			Wet solids.		Solid phases.
$D_r^\circ$ .	% by weight.		% by weight.		
	$\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	
1.183	17.86	—	31.68	—	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .
1.202	17.17	3.40	31.73	0.27	
1.205	16.61	5.01	31.76	—	
1.229	15.84	7.18	27.73	13.10	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4$ .
1.224	15.89	6.87	23.43	25.89	
1.221	16.07	6.32	14.35	46.86	
1.228	14.68	8.06	2.58	79.29	$\text{Na}_2\text{SO}_4$ .
1.222	12.68	10.80	0.61	93.18	
1.237	11.21	12.56	0.13	96.78	
1.241	10.04	14.51	0.99	90.79	$\text{Na}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.240	9.96	14.70	0.57	65.25	
1.241	9.96	14.67	0.44	48.28	
1.204	4.40	17.12	0.35	40.98	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.203	3.27	17.84	0.49	37.76	
—	1.63	19.71	0.47	35.80	

TABLE IV.  
Isotherm at 31°.

Solutions.			Wet solids.		Solid phases.
$D_4^\circ$ .	% by weight.		% by weight.		
	$\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	$\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	
1.202	20.60	—	31.42	—	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .
1.210	20.44	1.05	32.44	0.05	
—	19.57	3.04	29.64	0.87	
1.213	19.46	4.11	31.26	1.77	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4$ .
—	19.66	4.41	30.41	5.47	
1.229	19.33	4.04	27.41	14.89	
1.222	19.69	4.32	20.39	35.73	
1.228	19.42	4.20	11.47	63.46	
1.253	22.22	2.56	3.01	86.41	$\text{Na}_2\text{SO}_4$ .
1.214	18.69	4.79	3.57	82.00	
—	16.36	6.58	3.59	79.98	
1.214	14.39	8.59	2.19	86.79	
1.219	12.14	11.56	1.96	88.01	
1.228	9.83	14.46	1.27	89.72	$\text{Na}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
—	7.47	18.92	0.45	92.39	
1.248	6.97	19.47	1.37	85.68	
1.264	4.81	23.06	1.99	68.91	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.288	2.85	27.39	0.34	84.30	
1.290	2.31	28.65	0.15	64.25	
1.291	2.43	28.72	0.25	42.85	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .
1.294	1.47	29.15	0.27	41.88	
1.285	0.40	29.97	0.05	41.81	



solid phase. The relations are shown in Fig. 3 and need no discussion. At 40°, where only anhydrous sulphate can exist, there is again no discernible miscibility. At all three temperatures, the part of the system in which solid sulphide appears is so small that one cannot make definite assertions about the solid phase.

By the determination of temperature-time curves in slow cooling and heating of suitably chosen mixtures, the transition points were determined as set out in Table VI, together with the compositions of saturated solutions in equilibrium with the solids indicated in the

TABLE V.  
Isotherm at 40°.

Solutions.			Wet solids.		Solid phases.
$D_4^*$	N	% by weight. $\text{Na}_2\text{S}$	% by weight. $\text{Na}_2\text{SO}_4$		
1.248	25.09	—	31.04	—	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .
1.248	25.01	—	32.23	—	
1.238	24.06	0.49	32.37	trace	
1.238	23.93	0.88	32.94	0.05	
1.256	24.28	1.62	32.08	1.58	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4$ .
—	23.44	1.77	31.75	2.96	
1.248	23.72	1.90	31.25	5.63	
1.247	23.79	1.84	30.53	6.69	
1.253	23.62	1.90	27.57	16.59	$\text{Na}_2\text{SO}_4$ .
1.253	23.57	1.84	2.08	91.46	
1.241	23.25	1.79	1.69	93.25	
1.223	23.04	1.91	1.89	48.98	
—	22.30	1.94	3.04	86.67	
1.233	21.91	2.44	—	—	
1.233	21.99	2.45	2.39	87.39	
1.239	21.27	2.79	4.14	81.48	
1.228	20.91	3.04	2.28	89.18	
1.233	20.36	3.41	1.76	91.62	
—	14.08	25.22	0.78	95.43	
1.223	15.45	6.53	—	—	
—	14.97	7.37	1.90	89.62	
1.223	14.25	8.72	3.33	75.75	
1.220	14.31	8.17	—	—	
1.236	9.78	14.14	2.07	81.18	
—	9.49	15.23	1.89	82.58	
1.260	6.18	20.25	1.83	75.63	
—	3.56	24.43	0.78	80.90	
1.302	1.32	28.90	0.18	83.71	

TABLE VI.  
Transition points.

Transition.	Temp.	% by weight in soln.		$D_4^*$
		$\text{Na}_2\text{S}$ .	$\text{Na}_2\text{SO}_4$ .	
<i>Binary.</i>				
$\text{Na}_2\text{S} \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}.$	4.7° (h) } 4.7 (c) }	12.46	—	1.128
<i>Ternary.</i>				
Same in satd. $\text{Na}_2\text{SO}_4$ .	2.3 (h) } 2.3 (c) }	11.49	1.40	1.135
<i>Ternary.</i>				
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4$ in satd. $\text{Na}_2\text{S}$ .	20.9 (h) } 20.2 (c) }	13.41	9.48	—
?	29.6 (h) }	19.97	4.48	1.331
—	29.6 (c) }			
(h) = arrest on heating.		(c) = arrest on cooling.		

(h) = arrest on heating.

(c) = arrest on cooling.

first column. Sulphate lowers the transition point between deca- and nona-hydrates of the sulphide from 4.7° to 2.3°, whilst the transition point between decahydrated and anhydrous sulphates

may be reduced by sulphide from  $32.4^{\circ}$  to  $20.6^{\circ}$ . For small concentrations of sodium sulphide, the depression of this transition point has been measured and found to be directly proportional to the concentration of sulphide. It may be expressed by  $D = 0.625C$ , where  $D$  is the depression and  $C$  the concentration of sulphide in g. per 100 g. of solution.

A curious arrest at  $29.6^{\circ}$  (Table VI) has not been explained. The solution has a high density and the arrest may correspond with the formation of a metastable hydrate no trace of which was found in the work on the  $31^{\circ}$ -isotherm.

### *Summary.*

1. The system sodium sulphide-sulphate-water has been investigated between  $0.1^{\circ}$  and  $40^{\circ}$ .

2. Sodium sulphide has been found to form a decahydrate which has not been previously described. The transition point in the binary system between deca- and nona-hydrates is  $4.7^{\circ}$ .

3. Mutual miscibility is shown by the solid decahydrates of sulphide and sulphate at  $0.1^{\circ}$ .

4. At  $18^{\circ}$ ,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  can dissolve sulphate (as nonahydrate?) but neither  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  nor  $\text{Na}_2\text{SO}_4$  shows appreciable tendency to include sulphide in its crystals.

5. The transition point between deca- and nona-hydrated sulphides is lowered in the ternary system by sulphate to  $2.3^{\circ}$ ; while that between decahydrated and anhydrous sulphate is lowered by sulphide to  $20.6^{\circ}$ .

The author's best thanks are due to Professor A. C. D. Rivett for suggesting this investigation and for much helpful criticism.

UNIVERSITY OF MELBOURNE.

[Received, February 22nd, 1928.]

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## CXIX.—*The Constitution of Maltose.*

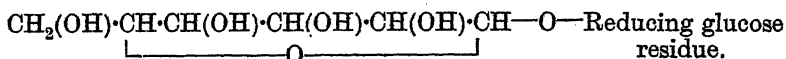
By JAMES COLQUHOUN IRVINE and IAN MACLEOD ARMSTRONG  
BLACK.

A CONSIDERABLE section of the work conducted in this laboratory on the constitution of polysaccharides has been withheld from publication for some years owing to the fact that the results could not be readily explained. As these discordant features accumulated, it became increasingly evident that current views regarding the structure of maltose required revision and that it was necessary to



study the problem anew. This we have done and, as our results differ fundamentally from those upon which the accepted structure for the disaccharide is based, it is desirable to review the whole situation.

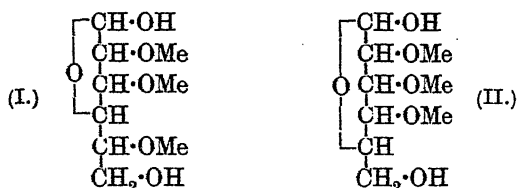
The first attempt to solve the constitution of maltose by means of methylation was made by Purdie and Irvine (J., 1905, 87, 1022), who applied the silver oxide reaction directly to the free sugar. Although the alkylation was complicated by oxidation of the reducing group, the decisive result emerged that, on hydrolysis of the product, crystalline tetramethyl glucose was produced. This revealed the structure of one-half of the maltose molecule which, on the basis of the amylene-oxide formula for glucose,\* becomes :



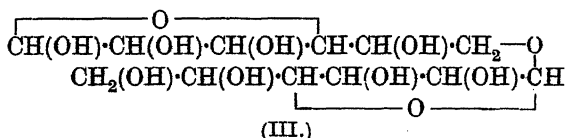
An attempt was subsequently made by Irvine and Dick (J., 1919, 115, 593) to determine the position through which the second glucose residue is attached, the scheme involving the complete methylation of methylmaltoside and the identification of the scission products. In this case an experimental obstacle intervened, it being found that the method employed to prepare methylmaltoside was accompanied by degradation of the sugar so that one of the hydrolytic products finally obtained consisted of a methylated pentose. The research was, however, of some value as, once more, crystalline tetramethyl glucose was isolated, thereby confirming the earlier result of Purdie and Irvine. Subsequently, Haworth and Leitch (J., 1919, 115, 809) applied the methyl sulphate reaction to maltose in two successive stages, the first being designed to convert the sugar into methylmaltoside, which was partly methylated in the second stage and thereafter fully alkylated. Hydrolysis of this product yielded two methylated glucoses, one of which, as was to be expected, was tetramethyl glucose. The object of the research was, however, to ascertain the structure of the *reducing* hexose residue in maltose, so that greater importance must be attached to the constitution of the remaining scission product, *viz.*, trimethyl glucose. The sugar isolated by Haworth and Leitch was a syrup and was stated by them to be the liquid variety of trimethyl glucose in which the terminal  $-\text{CH}_2\text{-OH}$  group is unsubstituted. As originally formulated, this sugar was described as 2 : 3 : 5-trimethyl

\* The amylene-oxide formula for glucose is applied in this paper only tentatively and is restricted to derivatives which are known to be convertible into crystalline tetramethyl glucose. The results now contributed show that it is inadvisable to go further.

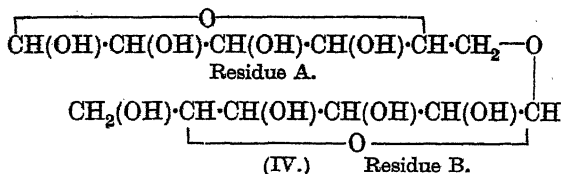
glucose (I), but adopting meanwhile the amylene-oxide structure, it may be termed 2 : 3 : 4-trimethyl glucose (II).



Irrespective of the oxygen-ring, the essential point is that the formation of such a sugar implies that the two hexose residues in the disaccharide are coupled through a terminal hydroxyl group. On this basis, Haworth and Leitch ascribed the following structure to maltose and applied, by analogy, a similar constitution to melibiose :



This formula has remained in use for the past seven years, but was modified recently (Charlton, Haworth, and Peat, this vol., p. 89) by the incorporation of an amylene-oxide linkage in each glucose residue, giving the structure :



Evidently the constitution as given above is valid only if each half of the molecule gives rise to the appropriate methylated glucose. With regard to residue B, this was already known from the results of earlier workers, and the additional experimental evidence contributed by Haworth and Leitch consisted in the isolation and identification of the trimethyl glucose derived from residue A. Considering the fundamental structural issues involved (which are by no means confined to maltose), it is of the utmost importance to know that the trimethyl glucose is actually what it was described to be. Our results, unfortunately, show that this is not the case. The trimethyl glucose obtained by us from maltose is the crystalline 2 : 3 : 6-isomeride, and not, as stated by Haworth and Leitch, the liquid 2 : 3 : 4-variety. The erroneous conclusion to which the latter workers came is in no way concerned with the position of the oxygen

ring in glucose or with a difference in the interpretation of results, but is attributable to failure to identify correctly the sugar actually formed. It is regrettable that correction should have been so long delayed, particularly as the constitutional formulæ of other disaccharides and of the polysaccharides based on glucose become involved in the fundamental error.

The evidence upon which Haworth and Leitch identified and ascribed a structure to the trimethyl glucose they obtained from maltose may be discussed. The sugar failed to solidify and was separated from tetramethyl glucose by distillation, a process of doubtful utility in any case where the presence of 2 : 3 : 4-trimethyl glucose might be expected. No crystalline derivative was prepared and the bulk of the material was subjected to oxidation by nitric acid, the product thus formed being described as a trimethyl saccharolactone since it corresponded in composition with such a compound. Inquiry into the particular method of oxidation employed has, however, shown that it is untrustworthy. We have ascertained that unchanged sugar may persist along with oxidation products and, in addition, the removal of nitric acid by evaporation with alcohol results in partial esterification of the oxidation acids. In consequence, the analytical results obtained on *undistilled* products are subject to serious errors. For example, a methyl group may be removed by oxidation from the terminal 6-position of the sugar chain, but an ethyl group may enter the carboxyl position, thus introducing compensation into the methoxyl determinations. We have encountered all of the above complications and may cite the oxidation of monomethyl glucose by nitric acid as a conspicuous, but by no means unique, example of a complex reaction which leads to a mixture of products displaying fortuitously the properties and composition of a simple lactone. This accounts for our recent practice in isolating oxidation products in the form of volatile esters or of crystalline derivatives.

Turning to other properties of the trimethyl glucose described by Haworth and Leitch, it may be mentioned that the specific rotations of the compound did not agree with those determined by previous workers (Irvine and Dick, *loc. cit.*) and failed to reveal the characteristic depression shown after distillation. Information was, in fact, available showing that it is impossible to identify 2 : 3 : 4-trimethyl glucose by observation of the activity of distilled specimens, as the value of the specific rotation may vary as much as 20° to 30° owing to the partial transformation of the dextrorotatory sugar into its levorotatory anhydride. This irregularity was encountered so far back as 1903 and was again emphasised by Irvine and Oldham (J., 1921, 119, 1754).

Consideration of the whole situation shows that the claims of Haworth and Leitch regarding the trimethyl glucose they obtained from maltose rested upon insecure experimental evidence which has not been supplemented as knowledge of methylated sugars increased. There can be no doubt that the material they described as the liquid form of trimethyl glucose was an impure specimen of the 2 : 3 : 6-isomeride, which failed to crystallise owing to the experimental treatment to which it had been subjected. In this connexion, Irvine and Hirst (J., 1922, 121, 1214) state "the capacity of this sugar (2 : 3 : 6-trimethyl glucose) to separate in the solid form is seriously affected by impurities and seems to be inhibited by thorough drying so that, on distillation, a viscous syrup is obtained which solidifies only after several weeks. Even gentle warming above the melting point is sufficient to impair crystallisation." The above statement, taken in conjunction with our experience of oxidations by means of nitric acid, shows that it is hazardous, without the most exhaustive confirmation, to claim that any preparation of a trimethyl glucose which fails to crystallise is the 2 : 3 : 4-isomeride.

In overturning a result upon which so many other constitutional formulæ depend, it has been necessary to exclude sources of error so far as they can be foreseen and to repeat the operations several times and by independent workers. Reference is made in the experimental part to some of the precautions adopted and to variations in the procedure. These fall under three main heads : (1) confirmation of the purity and uniformity of the maltose used, (2) variations in the method of methylation, (3) alternative methods of isolating the scission products. We employed three distinct samples of maltose, one of which was made in the laboratory during the War and was certified as conforming to bacteriological standards. With regard to the process of methylation, we followed in the first instance exactly the method described by Haworth and Leitch, applying the methyl sulphate reaction to the free sugar. In other experiments, methyl sulphate was used only until the product was soluble in chloroform, the methylation being completed by the silver oxide reaction alone. Despite these experimental variations, the same result was obtained, the product on isolation being a viscous syrup showing the properties ascribed by Haworth and Leitch to heptamethyl methylmaltoside.

It may be mentioned, however, that the methoxyl and carbon values determined on this material were consistently low, and that satisfactory analytical figures were obtained only when the initial material consisted of crystalline methylmaltoside. The hydrolysis proceeded normally, the liberated sugars being separated by extrac-

tion of an aqueous solution with chloroform. By this means it was possible to effect a sharp separation of the tetramethyl and trimethyl glucoses without distillation or heating above the melting points of these compounds. In all the experiments, both sugars crystallised and proved to be respectively 2 : 3 : 4 : 6-tetramethyl glucose and 2 : 3 : 6-trimethyl glucose. As a precautionary measure, we examined all the hydrolysis products to ascertain if any 2 : 3 : 4-trimethyl glucose was present, but no trace of this sugar could be detected.

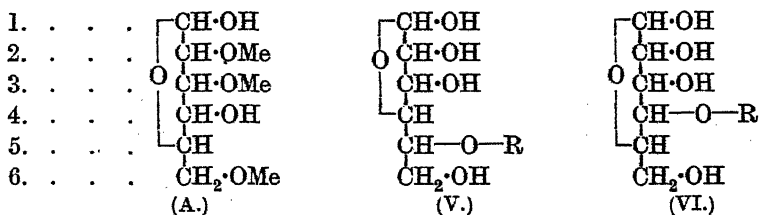
In order to place our procedure beyond question, we have duplicated the entire research, using pure  $\beta$ -methylmaltoside as the starting material. In this case also, the methylation was conducted in two ways, using either the silver oxide method or the methyl sulphate reaction throughout. Here again the same result was obtained, irrespective of the method employed, the hydrolysis of the compound giving, as before, crystalline tetramethyl glucose together with crystalline 2 : 3 : 6-trimethyl glucose free from the liquid isomeride. Finally, for the purposes of the present investigation, Irvine and Oldham prepared 2 : 3 : 4-trimethyl glucose by synthetical operations designed to leave the terminal  $\text{CH}_2\cdot\text{OH}$  group unsubstituted (J., 1925, 127, 2729). The product was entirely different from the isomeride obtained from maltose.

Considering the precautions adopted and the results of collateral investigations designed to test sources of error, we are convinced that maltose cannot be formulated in either of the ways suggested by Haworth. The necessity for correction is not limited to the single case of maltose, but extends to all constitutional schemes in which the maltose structure is either directly or indirectly involved. For example, with the displacement of maltose from the position it has hitherto occupied in the structural classification of the disaccharides, the following constitutional relationships must be again regarded as conjectural: (1) maltose and cellobiose, (2) maltose and gentiobiose, (3) lactose and melibiose (Haworth and Leitch, *loc. cit.*; J., 1918, 113, 188; Haworth and Hirst, J., 1921, 119, 193; Haworth and Wylam, J., 1923, 123, 3120).

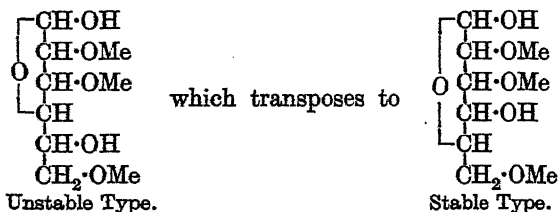
Further, speculations on the structure of isomaltose and of the molecular unit of starch, which have naturally been founded on a constitutional formula for maltose, lose their significance, a conclusion foreshadowed by results obtained in this laboratory on the methylation of starch and of the polyamyloses.

It would be premature, even with the additional information now available, to speculate as to the alterations in disaccharide formulæ which are now necessary, and discussion is limited to some general considerations. The question arises as to whether methylation

alters the linkage of one sugar residue with another, but this has already engaged our attention (Irvine and Oldham, J., 1925, 127, 2910), although the argument that maltose and cellobiose give rise to different methylated sugars no longer holds. There remains an analysis of how far conclusions as to structure are logically valid when based on the formation of 2:3:6-trimethyl glucose. This sugar, formulated as an amylene-oxide, may be represented as (A) and on first inspection it might appear that all disaccharides which yield this compound must have the glucose residues attached through position 4. But inspection will show that the number of diglucoses which qualify for this mode of linkage is now larger than stereochemical considerations accommodate. The situation thus created is disconcerting, but is greatly simplified when it is recognised that 2:3:6-trimethyl glucose is capable of reacting as a  $\gamma$ -sugar, this property of the compound having been already pointed out (Irvine and Hirst, *loc. cit.*). It follows that the production of 2:3:6-trimethyl glucose is not absolutely diagnostic in discriminating between positions 4 and 5 as the point of union of two glucose residues. Thus, if we imagine two disaccharides to be constituted as under (V and VI), where R represents the non-reducing hexose residue,



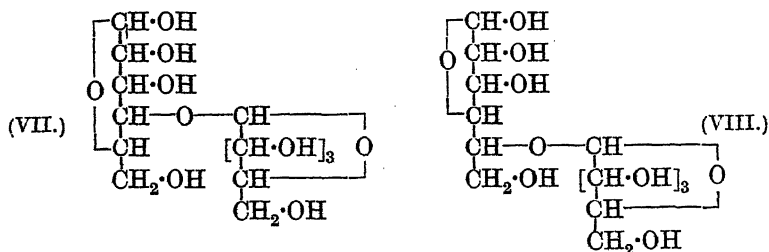
only the compound corresponding to (VI) would yield the stable form of trimethyl glucose directly. The other could, however, do so indirectly, giving in the first place:



The possibility thus revealed invests all such constitutional studies with precisely the same uncertainty as is encountered in the hydrolysis of sucrose and inulin. Evidently the disaccharides must be studied afresh in the light of the possibility that  $\gamma$ -oxidic or other

linkages may be present in one or other of the constituent sugars. These considerations have been made the subject of other investigations now in progress in this laboratory.

According to the evidence now submitted, maltose may be formulated either as :



The methylation process does not discriminate between these alternatives, one of which must represent cellobiose and isocellobiose, whilst the other must be reserved for maltose together with, presumably, isomaltose. The conversion of methylmaltoside into  $\beta$ -methylglucoside appears to favour the allocation of formula (VII) to maltose but, on the other hand, the degradation of maltose is more easily explained in terms of formula (VIII). Work is in progress to decide between the above alternatives.

The results now contributed serve to emphasise a view formerly expressed (Irvine, J., 1923, 123, 898) that no claim for finality can be made regarding the constitution of sugars and that each successive modification represents only a stage in knowledge.

## EXPERIMENTAL.

*Methylation of Maltose.*—In order to economise description, it may be stated that each method of alkylation now described was applied to three distinct specimens of maltose. Two of these were obtained from trustworthy manufacturing firms and were selected as they displayed the correct melting point and specific rotation for the disaccharide. The third specimen was prepared in this laboratory during the War and was subjected, before use, to a special bacteriological examination. It was presumably identical with the material used by Haworth and Leitch. The descriptions of the methylation now given apply therefore to six distinct preparations, and the results quoted are typical.

*Method I.* The directions given by Haworth and Leitch (*loc. cit.*, pp. 813—814) were adhered to in every detail. After three methylations by means of methyl sulphate, the product extractable with chloroform weighed 27.5 g. (from 30 g. of maltose) and contained 50.5% of methoxyl. On distillation, 19.5 g. of a viscous syrup were

obtained (b. p. 189—191°/0.2 mm.;  $n_D$  1.4685), but it may be noted that a small fraction of lower boiling point was also collected and that a viscous residue remained undistilled. The main fraction, on redistillation, boiled at 190°/0.2 mm. and showed  $[\alpha]_D$  in alcohol + 91.1° for  $c = 1.15$ ;  $[\alpha]_D$  in acetone + 92.1° for  $c = 1.256$ ; OMe, 50.4%;  $n_D$  1.4706. After another methylation, the product was separated on distillation into three portions, and, although the boiling point showed no variation, the second fraction (11.2 g.) was selected as being in best agreement with the constants quoted by Haworth and Leitch for heptamethyl methylmaltoside.

The methoxyl content was nevertheless slightly low, but purification was effected by solution in light petroleum and extraction with water. A small amount of discoloured syrup was retained in the hydrocarbon solvent, and the main product, when recovered from the water, was entirely decolorised by boiling in chloroform solution with norit. Average yield, 10 g. per 30 g. of maltose used. Found: C, 52.3; H, 8.6; OMe, 52.7. Calc. for heptamethyl methylmaltoside,  $C_{12}H_{14}O_3(OMe)_8$ , C, 52.9; H, 8.4; OMe, 54.6%;  $n_D$  1.4691;  $[\alpha]_D$  in acetone + 90.6° for  $c = 1.16$ . The maltose provided by manufacturing firms gave results corresponding closely with those described above, although the final yield of methylated maltoside was invariably smaller. The same tendency for the methoxyl value to be low was again observed, successive preparations showing OMe, 52.0 and 52.4, in place of the calculated value 54.6%.

*Method II.* The initial stages in the methylation were conducted as before and the product soluble in chloroform was isolated. Thereafter only the silver oxide method was applied, the following being an account of a typical case. 40 G. of the partly methylated maltoside were alkylated as usual with methyl iodide (6 mols.) and silver oxide (3 mols.), the treatment being continued for 8 hours. The yield of distilled material amounted to 32 g., of which 22 g. were collected at the boiling point of heptamethyl methylmaltoside. The undistilled residue was rejected and the distilled material was again methylated and fractionated. Finally, the middle fraction was redistilled and purified by solution in light petroleum and extraction with water as already described.

The heptamethyl methylmaltoside thus isolated was identical with that obtained by Method I and gave the same hydrolysis products, but the methoxyl content was again low (OMe, 52%) and the refractive index was 1.4700 in place of 1.4691.

*Hydrolysis of Heptamethyl Methylmaltoside.—Method A.* In studying this reaction the preparations of the alkylated maltoside obtained from different specimens of maltose were kept apart and treated separately; identical results were, however, obtained in each case.



The maltoside was hydrolysed by heating with 5% aqueous hydrochloric acid as described by Haworth and Leitch, but a variation was introduced into the method of separating the sugars, the acid liquor being extracted six times with chloroform. The syrup isolated from the chloroform solution crystallised at once and consisted of tetramethyl glucose.

The sugar remaining in the aqueous liquor was recovered in the usual manner and converted into the corresponding methylglucoside by boiling with methyl alcohol containing 1% of hydrogen chloride until the solution was devoid of reducing action. After rendering alkaline by the addition of sodium bicarbonate, the alcohol was removed and the residue taken up in water. On extracting six times with chloroform, the trimethyl methylglucoside passed into solution in the chloroform, from which it was recovered and purified by distillation at  $145^{\circ}/0.6$  mm. This treatment removed traces of impurity and the glucoside was then rehydrolysed with 5% aqueous hydrochloric acid. On isolation of the product in the usual manner, the trimethyl glucose was obtained as a viscous syrup which slowly crystallised in the manner characteristic of 2:3:6-trimethyl glucose. The sugar was recrystallised from ether and identified as afterwards described.

In order to secure control evidence, the above operations were conducted in lots of 10 g., a typical result being that 10.3 g. of heptamethyl methylmaltoside gave 4.7 g. of crystalline tetramethyl glucose and 4.7 g. of syrupy trimethyl glucose. The latter, in turn, yielded 3.6 g. of distilled trimethyl methylglucoside, from which 3.3 g. of the corresponding sugar were obtained.

*Method B.* The hydrolysis of heptamethyl methylmaltoside was in this case conducted under conditions which would convert the liberated sugars into the corresponding methylglucosides. This was effected by boiling with excess of methyl alcohol containing 1% of hydrogen chloride, it being found that, in the course of 7 hours' treatment, the specific rotation, which had gradually diminished, attained a constant value. Boiling was continued for an additional period of 5 hours, after which the acid was neutralised and the solvent alcohol removed. The residue was then dissolved in water and the solution extracted repeatedly with chloroform, a syrup being obtained on evaporating the latter solvent. This syrup was a mixture of tetramethyl and trimethyl methylglucosides which was purified from traces of extraneous products by distillation under diminished pressure. The total distillate was thereafter hydrolysed in the usual manner by means of aqueous hydrochloric acid and the two sugars thus formed were separated by extraction with chloroform as described in Method A. The results were as before, crystal-

line tetramethyl glucose being isolated from the chloroform solution and the aqueous liquor retaining trimethyl glucose. This was isolated initially as a syrup which crystallised on keeping. In this particular instance, the solidification of the sugar was complete only after an interval of 3 weeks owing, it would appear, to the presence of a small proportion of a very viscous syrup which was less soluble in ether and had a smaller methoxyl content than trimethyl glucose. The crystallisation of the sugar was delayed by cooling and proceeded more satisfactorily at room temperature.

*Examination of the Hydrolysis Sugars.*—*Identification of 2 : 3 : 4 : 6-tetramethyl glucose.* The identification of the tetramethyl glucose presented no difficulty. All the specimens were recrystallised three times from light petroleum. The composition, melting point, mixed melting point, and mutarotation determined on the product agreed exactly with the accepted standards for 2 : 3 : 4 : 6-tetramethyl glucose.

*Identification of 2 : 3 : 6-trimethyl glucose.* In the hydrolysis experiments already described, the trimethyl glucose was obtained as a crystalline mass which still retained a small quantity of a viscous syrup. The material was thoroughly incorporated with dry ether containing a little acetone, and the crop of crystals removed by filtration. On evaporation of the filtrate and extraction of the residue with ether any non-crystallisable syrup was left undissolved, while the extract gave further crops of crystalline sugar. In one instance, when the proportion of adhering syrup was larger than usual, it was removed by draining on porcelain, from which it was recovered and examined, with negative results, for 2 : 3 : 4-trimethyl glucose. Each preparation of the sugar was purified by recrystallisation from ether containing a small proportion of low-boiling petroleum. In this way, the compound was obtained in characteristic long needles melting at 113—114° and showing no depression of the melting point when mixed with a standard specimen of 2 : 3 : 6-trimethyl glucose (Found: OMe, 41.2. Calc., 41.9%). When dissolved in water the sugar displayed downward mutarotation, giving the equilibrium value  $[\alpha]_D^{20} + 70.9^\circ$ , the accepted permanent specific rotation for 2 : 3 : 6-trimethyl glucose being  $+70.5^\circ$ . The results quoted are typical of those obtained with all the specimens examined.

*Preparation of Methylmaltoside.*—In order to attain greater accuracy, the reactions of methylation and hydrolysis were duplicated using crystalline methylmaltoside as the starting material. As a number of interesting features were encountered in the preparation of methylmaltoside, these are referred to now, together with such practical details as we have found to be advantageous.

*Stage I.* The preparation of octa-acetyl maltose proceeds most satisfactorily when not more than 30 g. of maltose are used in each experiment. In successive preparations 300 g. of the sugar were converted into the acetate, each experiment yielding on an average 20 g. of product which had been recrystallised from alcohol until the m. p. was 158—159°.

*Stage II.* Trial experiments showed that the action of hydrogen bromide on octa-acetyl maltose gives the best results when carried out on small quantities of the order of 2 g. This may be increased to a maximum of 10 g. but, with larger quantities, degradation of the disaccharide takes place and serious difficulties are introduced into the purification of the acetylated methylmaltoside. By tedious repetition of the typical experiment now described, 250 g. of the octa-acetate were converted into hepta-acetyl methylmaltoside. 2 G. of octa-acetyl maltose were dissolved in 50 c.c. of a mixture consisting of glacial acetic acid saturated with hydrogen bromide (10%), of ether (15%), and of benzene (75%). The use of this particular mixture of solvents secures a permanently clear solution which enables the reaction to be followed by reliable polarimetric readings. The rotation of the solution came to a constant value in about 12 hours, the final specific rotation, recalculated for the change of concentration, ranging between + 184° and + 190°. The solution was washed twice with water and dried over anhydrous sodium sulphate, the solvent being thereafter removed. The residual syrup was dried in a vacuum at a temperature not exceeding 55°, a process which was accompanied by vigorous frothing.

*Stage III.* The bromo-derivative was dissolved by shaking with anhydrous methyl alcohol in the presence of silver carbonate, mixing being conducted on a mechanical shaker until a test sample of the solution was free from bromine. At this stage crystals of the product usually separated and consequently both the silver residues and the filtrate were extracted with hot chloroform. On removal of the solvent, hepta-acetyl methylmaltoside remained as a syrup which crystallised readily and was purified from absolute alcohol. In the course of 10 parallel preparations it was found that, as a rule, three crystallisations from alcohol gave a product melting at 124—125°, but, by repeating the crystallisation, this value could be raised to 128—129° (Found: C, 49.8; H, 5.9; OMe, 4.5. Calc., C, 49.8; H, 5.8; OMe, 4.8%.  $[\alpha]_D$  in chloroform + 53° for  $c = 1.5$ ). This melting point is identical with that quoted by Koenigs and Knorr, who prepared the compound from the corresponding nitrate. The loss sustained in these recrystallisations is considerable, as only about 40% of the original material is obtained in the pure condition.

In addition, a second crystalline product was isolated in amounts which varied in different preparations and it may be noted that when this substance was present in large proportion it was impossible to separate it from hepta-acetyl methylmaltoside by ordinary fractional crystallisation. Normally, this by-product was deposited from the mother-liquors, accumulated in the course of recrystallising hepta-acetyl methylmaltoside, when kept in a cool place. After recrystallisation from alcohol the compound melted at 145–146°, and showed  $[\alpha]_D$  in chloroform + 69.1° for  $c = 1.5$  (Found: OMe, 5.2;  $\text{CH}_3\text{-CO}_2\text{H}$ , 63.3. Calc. for  $\text{C}_{24}\text{H}_{34}\text{O}_{16}$ , OMe, 5.4;  $\text{CH}_3\text{-CO}_2\text{H}$ , 62.3%). The examination in detail of this compound will form the subject of a later communication.

*Stage IV.* Hepta-acetyl methylmaltoside, in quantities of about 40 g., was dissolved in a large excess of absolute alcohol saturated with dry ammonia. After 2 days, the rotation of the solution became constant and thereafter the solvent was removed under diminished pressure. The viscous syrup then remaining was dissolved in the minimum amount of alcohol and the methylmaltoside precipitated by the addition of small quantities of a mixture of chloroform and ether. The product was thereafter repeatedly recrystallised from a mixture of alcohol and ethyl acetate—a process which, if wasteful, is necessary before the maximum melting point of 110–111° is attained. Average yield, 9.5 g. In this condition, methylmaltoside contained 1 molecule of combined water (Found: OMe, 8.3;  $\text{H}_2\text{O}$ , 4.9. Calc. for  $\text{C}_{13}\text{H}_{24}\text{O}_{11}\cdot\text{H}_2\text{O}$ , OMe, 8.3;  $\text{H}_2\text{O}$ , 4.8%).

The following observations were made on a specimen dried over phosphoric anhydride at 100°/15 mm.: C, 43.8; H, 7.0. Calc. for  $\text{C}_{13}\text{H}_{24}\text{O}_{11}$ , C, 43.8; H, 6.75%.  $[\alpha]_D$  in alcohol + 63.5° for  $c = 1$ ; in water, + 83.9° for  $c = 1$ .

*Methylation of Methylmaltoside.*—This methylation was carried out by the silver oxide reaction in a manner parallel with that employed in the case of methylglucoside. In the first three methylations it was necessary to use methyl alcohol as an extraneous solvent, but thereafter the material was freely soluble in methyl iodide alone. After the sixth methylation, the refractive index was 1.4689 and the methoxyl content 50.1%. Two additional methylations failed to alter  $n_D$ , although the methoxyl content had increased to 52.3%. On distillation in a high vacuum, no lower-boiling distillate was obtained and the material distilled sharply at the boiling point of heptamethyl methylmaltoside (Found:  $n_D$ , 1.4662; yield, 76%; C, 52.7; H, 8.45; OMe, 54.1. Calc. for  $\text{C}_{20}\text{H}_{38}\text{O}_{11}$ , C, 52.9; H, 8.4; OMe, 54.6%).

Solvent.	c.	$[\alpha]_D$ .
Water .....	0.508	+88.1°
Alcohol .....	0.562	81.9
Chloroform .....	0.557	78.9
Acetone .....	0.577	78.1

*Hydrolysis of Heptamethyl Methylmaltoside.*—A 4.5% solution of the compound in 5% aqueous hydrochloric acid was boiled until the rotation, which at first diminished, increased to a constant value. Judging from the initial polarimetric reading, it would appear that hydrolysis commenced in the cold.

Time. ( $l = 1$ ).	a.	$[\alpha]_D$ .
Start .....	+3.11°	+69.3°
15 mins. boiling .....	2.68	59.6
1 hour's " .....	2.85	63.4
2½ " " .....	3.27	72.3 constant.

After neutralising the solution with barium carbonate it was decolorised with norit and extracted six times with chloroform. The extract gave crystalline tetramethyl glucose (yield, 91% of the theoretical amount). Trimethyl glucose was recovered from the aqueous liquor by evaporation and extraction of the residue with acetone. Removal of this solvent left a syrup which was taken up in ether containing a trace of acetone and treated as already described. The trimethyl glucose crystallised rapidly, solidification beginning spontaneously in a few hours (yield, 87% of the theoretical amount).

*Tetramethyl glucose.* After two recrystallisations, m. p. 93–95°;  $[\alpha]_D$  in absolute alcohol +112.1° (initial)  $\rightarrow$  83.4° (constant).

*Trimethyl glucose.* After two recrystallisations, m. p. 113–114°; mixed m. p. 113–114°; permanent specific rotation in water +70.2°; OMe, 41.6%. All the above determinations agree exactly with the standard values for 2 : 3 : 6-trimethyl glucose and further confirmation was obtained by converting the sugar into the corresponding  $\beta$ -methylglucoside. This proved to be identical with the trimethyl methylglucoside obtained from cellulose; m. p. 57.5°; mixed m. p. 57°; C, 50.6; H, 8.4; OMe, 51.9. Calc., C, 50.8; H, 8.5; OMe, 52.5%. The specific rotation in methyl alcohol for  $c = 1$  was –29.3°.

The thanks of the authors are due to the Carnegie Trust for a Research Fellowship held by one of them, and also to Dr. J. W. H. Oldham and to Mr. C. B. Purves (Carnegie Fellows) for much valuable help in carrying out control experiments.

CXX.—*The Constitution of the Disaccharides. Part X. Maltose.\**

By CONRAD J. ASTLEY COOPER, WALTER NORMAN HAWORTH,  
and STANLEY PEAT.

THE investigation of the structure of maltose by Haworth and Leitch (J., 1919, **115**, 809) was one of the earliest of those undertaken in the disaccharide series. In the interval which has elapsed, greater familiarity with the properties and mode of identification of the partly methylated glucoses, and particularly of the trimethyl glucoses, has been gained.

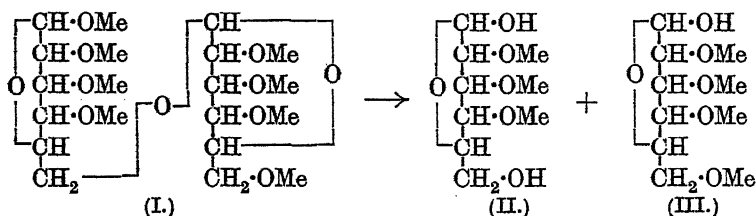
During a research, which will shortly be published, on the constitution of Ling and Nanji's isomaltose (J., 1923, **123**, 2666), certain irregularities were revealed which led us to suspect the accuracy of the formula previously applied to maltose. Consequently, the study of the latter sugar has been again undertaken during the past 18 months, with results which seem to require a modification of Fischer's formula for maltose, which was supported by the work of Haworth and Leitch.

In the earlier paper, the structural formula which appeared to represent maltose showed the linking of the two hexoses as occurring through the primary alcohol residue of one hexose with the reducing group of the second. The experimental data on which this conclusion was based were dependent on the recognition of the structure of the trimethyl glucose (II) obtained, along with tetramethyl glucose (III), by hydrolysis of heptamethyl methylmaltoside (I). In these formulæ the revised structure for normal glucose is used (Charlton, Haworth, and Peat, this vol., p. 89); consequently the older 2 : 3 : 5-trimethyl glucose is now written as 2 : 3 : 4-trimethyl glucose.

The facts available at that time pointed to the non-identity of this specimen of trimethyl glucose, which was a liquid, with crystalline 2 : 3 : 6-trimethyl glucose, which was isolated as a hydrolysis product of methylated cellobiose (Haworth and Hirst, J., 1921, **119**,

\* Almost the whole of the experimental results given in this paper were obtained during the early part of 1925, but publication was held over for the inclusion of other confirmatory details. A private communication from Sir James Irvine was received on February 23th, 1926, intimating, but without experimental details, that he had communicated a paper to the Society announcing the isolation of 2 : 3 : 6-trimethyl glucose as a hydrolysis product of methylated maltose. In the circumstances, we consider it is advisable now to submit our results for publication, inasmuch as they may serve to confirm and supplement those obtained by Irvine and his collaborators, whose priority we acknowledge.

193). Moreover, the oxidation of the trimethyl glucose derived from methylated maltose led to the isolation of what was considered to be a trimethyl saccharolactone (IV), and for these reasons, since the primary alcohol residue had apparently undergone oxidation to a carboxyl group without loss of a methoxyl residue, the specimen of trimethyl glucose was considered to have three methoxyl residues in the 2 : 3 : 4-positions, as shown in formula (III).



In a new series of experiments, the whole of the early work was repeated, and gave identical analytical results for the oxidation product of the trimethyl glucose. The method of isolating the trimethyl glucose was then modified, and instead of separating the hydrolysis products of methylated maltose by distillation, the aqueous solution containing the methylated hexoses was repeatedly extracted with chloroform, which entirely removed tetramethyl glucose as the normal crystalline variety (2 : 3 : 4 : 6).

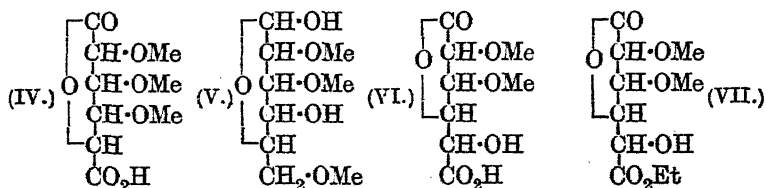
Remaining in the aqueous solution was the trimethyl glucose, and this was recovered by evaporation followed by extraction. The extracted syrup spontaneously crystallised, and yielded about 6% of the total in the form of the readily identifiable 2 : 3 : 6-trimethyl glucose. This was similar in all respects to the specimen previously isolated both from methylated cellobiose and from methylated lactose. Moreover, the remaining syrup appeared to consist of the  $\beta$ -form of this normal sugar, and probably contained also  $\alpha$ - and  $\beta$ -forms of the corresponding  $\gamma$ -sugar, into which the normal variety appears to pass somewhat readily owing to the presence of a free hydroxyl group in the  $\gamma$ -position in the chain. Possibly owing to the latter consideration, crystalline 2 : 3 : 6-trimethyl glucose cannot be isolated in quantity.

An alternative interpretation to that given in the earlier paper by Haworth and Leitch can now be offered, inasmuch as, accepting the trimethyl glucose as in reality 2 : 3 : 6-trimethyl glucose (V), this could pass on oxidation to dimethyl saccharolactone (VI). Under the experimental conditions described by Haworth and Leitch, the oxidation product from the trimethyl sugar was digested with ethyl alcohol for the purpose of removing traces of water, and it would appear to have undergone partial transformation

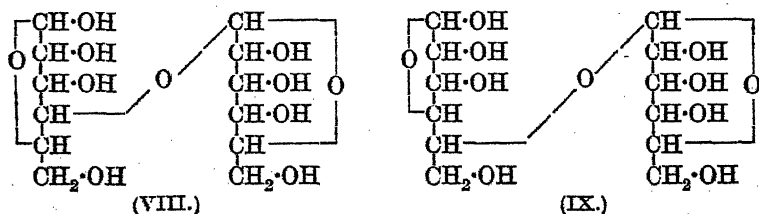
into the ethyl ester of the dimethyl saccharolactone. The analytical data previously quoted are given in column 1, and those of dimethyl saccharolactone (VI) and its ethyl ester (VII) in columns 2 and 3. The mean of the latter two results, given in column 4, will be seen to be closely similar to the analytical data previously interpreted under column 1 as indicating the constitution of the product as that of a trimethyl saccharolactone.

	1.	2.	3.	4.
C .....	46.03	43.6	48.4	46.0
H .....	6.26	5.45	6.46	5.95
OMe .....	35.9	28.2	37.5	32.85

In order to test this explanation, we have again oxidised the liquid portion of the trimethyl glucose and submitted this to esterification with ethyl alcohol containing hydrogen chloride. The main fraction isolated from this treatment distilled at 110–115°/0.03 mm. and gave titration results which corresponded to those required for compound (VII).



The valuable method of identifying 2:3:4-trimethyl glucose through its crystalline  $\beta$ -glucoside (Irvine and Oldham, J., 1921, 119, 1758) was not known at the time when the maltose paper was published and consequently we were unable then to apply this method of diagnosis. It seems clear, however, that 2:3:4-trimethyl glucose cannot be one of the hydrolysis products of methylated maltose, inasmuch as the specimen in our possession has since failed to satisfy those tests. The  $\beta$ -glucoside, when prepared, did not crystallise on keeping or on nucleation with specimens of 2:3:4-trimethyl  $\beta$ -methylglucoside which had been isolated for purposes of



diagnosis during our work on the constitution of gentiobiose and of amygdalin biose. On the other hand, the isolation of crystalline



2:3:6-trimethyl glucose points to the necessity of revising the structural formula of maltose, to which is now given the constitution (VIII) or (IX). The formula (VIII) differs stereochemically but not structurally from that of cellobiose, since the latter is a glucose  $\beta$ -glucoside and maltose is a glucose  $\alpha$ -glucoside.

The adjustment of the formula of maltose removes many outstanding anomalies as to the behaviour of starch.

#### EXPERIMENTAL.

*Hydrolysis of Heptamethyl Methylmaltoside. Isolation of 2:3:6-Trimethyl Glucose and 2:3:4:6-Tetramethyl Glucose.*—A specimen of heptamethyl methylmaltoside (39.5 g.) prepared as previously described by Haworth and Leitch (*loc. cit.*) (b. p. 201—203°/0.03 mm.) was hydrolysed by digesting with 5% hydrochloric acid at 85° for 1½ hours and at 100° for a further period of 1½ hours. Thereafter the specific rotation of the solution remained constant, and the hydrolysis was complete. The neutralised solution was slightly concentrated under diminished pressure and extracted several times with large quantities of chloroform. The chloroform extract was dried and evaporated; the residual syrup crystallised almost immediately, yielding pure 2:3:4:6-tetramethyl glucose (16.5 g.).

The residual aqueous solution was completely evaporated under diminished pressure and gave a syrup (15 g.) which, on keeping for several weeks, partly crystallised. These crystals (m. p. 106—117°) were drained on porous tile, and purified by solution in dry ether, from which small, colourless needles separated in three fractions: (a) m. p. 105—111°; (b) 108—115°; (c) 102—109°. Further recrystallisation gave crystals (1.25 g.), m. p. 110—116°, which, in admixture with a specimen of 2:3:6-trimethyl glucose derived from methylated lactose (Haworth and Leitch), showed no depression of melting point. It showed in methyl alcohol ( $c = 1.73$ )  $[\alpha]_D +102.6^\circ$  after 15 minutes, changing to  $70.2^\circ$  after 12 hours, and, after catalysis, to  $67.5^\circ$  (Found: C, 48.4; H, 8.3; OMe, 40.4. Calc., C, 48.6; H, 8.1; OMe, 41.9%).

The uncrystallisable syrup from which the above crystals had been obtained was oxidised by digestion with nitric acid ( $d\ 1.2$ ), heating to 80° until brown fumes began to be evolved, and thereafter at 70° for 5½ hours. After being cooled and tested for the presence of free sugar, the solution was again heated for a short period until the whole of the sugar was oxidised. The nitric acid was then removed by distillation under diminished pressure at 35°, water being constantly added during this operation. Finally, the whole of the water was evaporated, and the syrupy residue dissolved in ethyl alcohol containing 2% of hydrogen chloride. This solution

was boiled for 8 hours in order to complete the esterification, and the product was isolated in the usual manner. The methoxyl and ester groups were determined by the Zeisel method, calculating both OMe and OEt in terms of OMe, and showed 40·6%. The ester was then distilled, the first portion being collected at 88—95°/0·03 mm., but the main portion, the analysis of which is given below, distilled at 110—115°/0·03 mm. (Found: OR, 39·3. Calc. for the ethyl ester of dimethyl saccharolactone,  $C_{10}H_{16}O_7$ , 37·5%).

*Titration.* 0·1108 G. required 4·7 c.c. of *N*/10-sodium hydroxide in the cold, and on heating in a water-bath with excess of the alkali for 20 minutes, a total of 8·81 c.c. of *N*/10-sodium hydroxide was required. Calculated for the ethyl ester of dimethyl saccharolactone,  $C_{10}H_{16}O_7$ , 8·92 c.c., and for the trimethyl saccharolactone,  $C_9H_{14}O_7$ , 9·46 c.c. Hydrolysis of this ester gave dimethyl saccharolactone (Found: OMe, 27·8. Calc.: OMe, 28·2%).

On another occasion, the whole of the work described in the paper by Haworth and Leitch (*loc. cit.*) on the constitution of maltose was repeated in every detail, and the lactone derived from the oxidation of trimethyl glucose was titrated and gave the following results: 0·0979 g. required 8·37 c.c. of *N*/10-sodium hydroxide. Calculated for trimethyl saccharolactone,  $C_9H_{14}O_7$ , 8·33 c.c. In the earlier paper, a small typographical error appeared in the account given of the titration results, and the above re-determination was therefore carried out. This anomaly is explained in the introduction.

The authors express their thanks to the Department of Scientific and Industrial Research for the award of a grant to one of them.

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## CXXI.—*Synthesis of Derivatives of $\gamma$ -Xylose.*

By WALTER NORMAN HAWORTH and GEORGE CRONE WESTGARTH.

THIS investigation forms a part of a general study of the constitution of the normal and the  $\gamma$ -forms of the sugars. The isolation of derivatives of  $\gamma$ -fructose,  $\gamma$ -galactose, and  $\gamma$ -arabinose encouraged the view that the existence of  $\gamma$ -forms was a general property of the sugars (Haworth and Law, J., 1916, 109, 1314; Haworth, Ruell, and Westgarth, J., 1924, 125, 2468; Baker and Haworth, J., 1925, 127, 365).

In the present paper, another example in the pentose series is

described, namely, *trimethyl  $\gamma$ -xylose*, the structure of which has been investigated by conversion into its lactone and comparison of the properties of the latter with the corresponding lactone which we have isolated from normal trimethyl xylose.

In the case of xylose, the condensation with methyl alcohol in the cold proceeds very tardily, the  *$\gamma$ -methylxyloside* requiring 5 to 7 days for its formation, as contrasted with fructose, which condenses with methyl alcohol in the course of  $\frac{1}{2}$  hour, and galactose and arabinose, which require a period of less than a day after solution of the sugar. In following the formation of the  *$\gamma$ -methylxyloside* polarimetrically, it was observed that the condensation was accompanied by no inversion in the sign of rotation, and indeed, the final value recorded,  $[\alpha]_D + 28.8^\circ$ , differed very little from the initial value,  $+ 28.3^\circ$ , of the original xylose solution, although intermediate readings attained a maximum of  $+ 37.7^\circ$ .

*$\gamma$ -Methylxyloside* is comparable in its properties with  *$\gamma$ -glucosides* in general, exhibiting the usual ease of hydrolysis with acids of extreme dilution, and the characteristic instability in presence of neutral permanganate. From the specimen of  *$\gamma$ -methylxyloside*, the completely methylated derivative, *trimethyl  $\gamma$ -methylxyloside*, was obtained as a colourless liquid,  $[\alpha]_D = + 32.0^\circ$  in methyl alcohol. Hydrolysis of this compound was effected at  $100^\circ$  with either *N/50-* or *N/100-hydrochloric acid*, but for the purpose of the preparation of the corresponding free sugar *N/15-acid* may conveniently be used, the hydrolysis being complete in 4 hours. The rotation changes accompanying the hydrolysis exhibited the usual fall and rise in value, giving a time-period curve characteristic of the  *$\gamma$ -glucosides*, and indicating the presence of two stereochemical forms.

Trimethyl  *$\gamma$ -xylose* was thus isolated as a liquid containing both  $\alpha$ - and  $\beta$ -forms, and its properties were compared with those of the normal trimethyl xylose prepared by Carruthers and Hirst (J., 1922, 121, 2306).

Trimethyl $\gamma$ -xylose.		Normal trimethyl xylose.
Syrup, b. p. $110^\circ/0.04$ mm.		Crystalline, m. p. $87-90^\circ$ .
$[\alpha]_D$	$+ 24.7^\circ \rightarrow 31.2^\circ$ .	$+ 74^\circ \rightarrow 21^\circ$ .
Action of permanganate.	Reduces vigorously.	No action.
Acid methyl alcohol.	Combines rapidly.	Combination slow.

It is noteworthy that these two structurally different forms should display specific rotations of the same sign and of similar magnitude. In this respect, the two varieties of trimethyl xylose may be compared with those of tetramethyl mannose, the  *$\gamma$ -form*

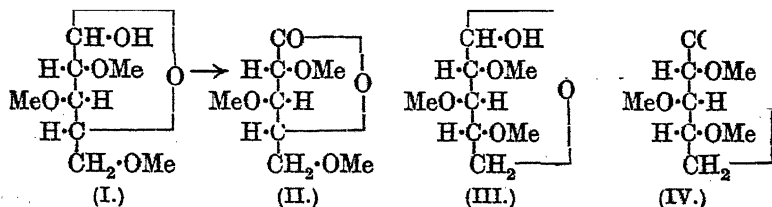
of which is crystalline and shows  $[\alpha]_D + 48.5^\circ$ , whereas the normal form is a liquid, showing  $[\alpha]_D + 17.2^\circ$  (equilibrium in methyl alcohol) (Irvine and Burt, J., 1924, 125, 1343).

With the object of deriving the constitution of trimethyl  $\gamma$ -xylose, the sugar was oxidised to the corresponding lactone, and for the purposes of comparison a similar procedure was followed also with the normal sugar. The properties of the two lactones are indicated below :

Lactone from	(a) Trimethyl $\gamma$ -xylose. Liquid.	(b) Normal trimethyl xylose. Crystalline, m. p. $55^\circ$ .
$[\alpha]_D$ in water.	$+74.1^\circ \rightarrow 61.4^\circ$ (Period, 21 days).	$-3.8^\circ \rightarrow +20.8^\circ$ (Period, 8 days).

A comparison of these rotation values indicates that the lactone from the  $\gamma$ -sugar resists hydrolysis to a much greater extent than the corresponding lactone from the normal sugar, and curves representing these changes have been given in the paper by Charlton, Haworth, and Peat (this vol., p. 93).

Since the constitution (III) allocated to normal trimethyl xylose on the basis of its oxidation to trimethoxyglutaric acid is that of a normal or  $\delta$ -oxide (Hirst and Purves, J., 1923, 123, 1352), it is evident that the structure of the derived lactone is that indicated by formula (IV). We are able to assign the structural formula (II) to the lactone from the  $\gamma$ -sugar for two reasons: (a) Its lactone ring must be situated on the right of the carbon chain on the basis of Hudson's rule, since the substance displays dextrorotation, diminishing in magnitude as the ring opens by hydrolysis to the hydroxy-acid. The lactone ring cannot engage the  $\beta$ -carbon acid, since in this case the lactone would be *lævorotatory*. (b) Its speed of hydrolysis in water is comparable in every respect with the series of  $\gamma$ -lactones examined by Charlton, Haworth, and Peat (*loc. cit.*). We therefore ascribe the constitution of a  $\gamma$ -lactone to this compound (II), whence it follows that the related sugar, trimethyl  $\gamma$ -xylose, has the constitution (I).



#### EXPERIMENTAL.

*Preparation of  $\gamma$ -Methylxyloside.*—Polarimetric observations indicated that at  $15^\circ$  solutions of xylose (2%, 3.5%, and 5%) in dry,

acetone-free methyl alcohol containing 1% of hydrogen chloride attained a maximum rotation after 25–30 minutes from the time of solution, this stage being succeeded by a slow diminution of rotation, and the equilibrium period seemed to be reached in about 24 hours.

The following values were obtained, for example, with a solution of this nature containing 2% of xylose :

Time (mins.) .....	5	10	15	20	30	53	58
$[\alpha]_D$ .....	+28.3°	35.3°	37.2°	37.4°	37.7°	36.1°	35.9°
Time (mins.) .....	163	210	22½ hrs.				
$[\alpha]_D$ .....	+30.9°	29.0°	28.8°				

With a similar solution containing, however, 5% of xylose, the following polarimetric figures were recorded :

Time (mins.) .....	20	26	36	52	62	72	112
$[\alpha]_D$ .....	+37.9°	38.6°	38.8°	38.5°	37.5°	37.0°	35.3°
Time (mins.) .....	167	262	397				
$[\alpha]_D$ .....	+33.5°	32.1°	30.3°				
Time (hours) .....	25	50	75				
$[\alpha]_D$ .....	+29.3°	28.5°	28.2°	(Thereafter, apparently constant.)			

The evidence furnished by tests with Fehling's solution, and also by actual isolation of the product, indicated that xyloside formation was far from complete at the end of these periods.

It thus appeared that glucoside formation proceeded very slowly under these conditions, xylose differing markedly in this respect from fructose, galactose, and arabinose. Moreover, the apparent attainment of a constant rotation after 24 hours was deceptive, in that methylxyloside continued to be formed even after 5 days, although the rotation changes were negligible during this extended period.

The following experimental conditions were therefore adopted for the preparation of larger quantities of  $\gamma$ -methylxyloside : Dried, finely-sieved xylose (11.9 g.) was dissolved in 238 g. of pure dry methyl alcohol containing 2.27 g. of hydrogen chloride, making a 5% solution of xylose in methyl alcohol containing 1% of hydrochloric acid. The mixture was kept at room temperature until it no longer reduced Fehling's solution, this stage being reached after 7 days. The product, isolated in the usual manner, was extracted with ethyl acetate, and consisted of a viscid syrup (8 g.) containing 0.7 g. of xylose crystals, which were removed by solution of the syrup in absolute alcohol. Distillation of the syrup was effected without any decomposition, giving rise to a pale yellow, viscid product, b. p. 161.5°/0.03 mm.,  $[\alpha]_D = +62.8^\circ$  in ethyl alcohol [Found : OMe, 18.4.  $C_5H_9O_4(OMe)$  requires OMe, 18.8%].

In another preparation of  $\gamma$ -methylxyloside, 27.5 g. of xylose

gave 20.6 g. of a syrup from which 15.8 g. of the distillate were obtained, the still residue being 3.4 g. In this experiment, the solution ceased to reduce Fehling's solution after 5 days.

*Methylation of  $\gamma$ -Methylxyloside.*—Methylation of this product was carried out with methyl sulphate and sodium hydroxide, care being taken to prevent development of acidity during the operation. The first eighth of each reagent was added at 40°, the second at 55°, and the remainder at the usual temperature of 70°. The quantities used were:  $\gamma$ -methylxyloside, 6.3 g.; methyl sulphate, 16.3 c.c.; sodium hydroxide, 15.5 g. in 31 c.c. of water. This yielded a pale liquid product which was remethylated with methyl iodide and silver oxide. The liquid product weighed 3.5 g. and had b. p. 78°/0.03 mm.,  $n_D = 1.4407$ . A small quantity of crystals was also collected.

The distilled liquid was colourless and immediately reduced neutral permanganate in the cold, but showed no reduction of Fehling's solution even on vigorous boiling [Found: C, 51.35; H, 8.4; OMe, 56.3.  $C_5H_6O(OMe)_4$  requires C, 52.4; H, 8.7; OMe, 60.2%.  $C_5H_7O_2(OMe)_3$  requires C, 50.0; H, 8.3; OMe, 48.3%].

These figures indicated that the xylose compound contained between three and four methoxyl groups.

The material was mixed with a further 11.2 g. which had been methylated to the same stage, and the whole (14.4 g.) was remethylated six times by Purdie's reagents. On distillation the first few drops were rejected, and a yield of 10.05 g. of the main fraction, b. p. 82.5–84.5°/0.03 mm., was obtained. In order to ensure a better fractionation, this product was re-distilled in the vacuum of the water-pump and then had b. p. 110–114°/14 mm. (Found: C, 52.2; H, 8.8; OMe, 59.0.  $C_5H_{18}O_5$  requires C, 52.4; H, 8.7; OMe, 60.2%).  $[\alpha]_D = +32.0^\circ$  in methyl alcohol ( $c = 0.7975$ );  $n_D 1.4387$ .

The sugar derivative was therefore a fully-methylated pentoside, and was essentially trimethyl  $\gamma$ -methylxyloside.

*Preliminary Hydrolysis.*—Preliminary experiments were instituted with the view of determining the ease of hydrolysis of trimethyl  $\gamma$ -methylxyloside with acid of varying dilutions. For this purpose hydrochloric acid (a) *N*/100; (b) *N*/50; (c) *N*/15 was employed at 100° and the following polarimetric data were recorded :

(a) Time (mins.) ...	5	25	55	85	120	150	210	275
$[\alpha]_D$ .....	+37.9°	17.2°	16.3°	19.7°	22.0°	24.1°	28.6°	33.2°
(b) Time (mins.) ...	3	27	57	89	109			
$[\alpha]_D$ .....	+33.9°	18.2°	24.2°	24.2°	26.4°			
(c) Time (mins.) ...	0	30	60	150	240	360		
$[\alpha]_D$ .....	+35.6°	28.8°	34.2°	36.9°	38.3°	37.8°		

To the solution (c) sufficient concentrated hydrochloric acid was added to increase the *N*/15-acid to 1% strength, and this solution was kept at 100° for an hour, after which the specific rotation diminished from +37.8° to 35.1°. By increasing the acid concentration to 5% and boiling the solution for a further period of 1½ hours the rotation fell to +29.9°. It was evident, therefore, that if any of the normal form of trimethyl methylxyloside was present in the original product, this quantity was extremely small, since normal trimethyl xylose has a lower specific rotation ( $[\alpha]_D + 21^\circ$ ) and is formed from its glucoside by hydrolysis with 5% hydrochloric acid at 100°.

*Isolation of Trimethyl  $\gamma$ -Xylose.*—Trimethyl  $\gamma$ -methylxyloside (4.5 g.) was dissolved in 100 c.c of *N*/15-hydrochloric acid and heated under reflux on a boiling-water bath as in the above control experiment. The hydrolysis was arrested after 5 hours, when a constant rotation was reached. The solution was then neutralised with barium carbonate, filtered, and evaporated at 40°/12 mm. to a syrup. This was dissolved in chloroform, filtered from inorganic salt and evaporated, and the residual product (3.8 g.) was distilled.

Fraction 1. B. p. 96.5°/0.06 mm., 1.3 g.,  $n_D = 1.4509$ .

„ 2. B. p. 110°/0.04 mm., 2.3 g.,  $n_D = 1.4539$ .

The first fraction contained some unchanged xyloside, and any of the normal form of trimethyl methylxyloside which might be present would be collected in this fraction of lower boiling point since it would be unaffected by the *N*/15-acid.

The second fraction, consisting of trimethyl  $\gamma$ -xylose (Found: C, 49.5; H, 8.5; OMe, 47.2.  $C_8H_{16}O_5$  requires C, 50.0; H, 8.3; OMe, 48.4%), was a colourless liquid which reduced Fehling's solution very actively, and also neutral permanganate in the cold.  $[\alpha]_D$  in water, +24.7°  $\rightarrow$  29.5° after 40 hours. After catalysis, the final equilibrium value was +31.2°.

*Oxidation of Trimethyl  $\gamma$ -Xylose with Bromine Water. Isolation of Trimethyl  $\gamma$ -Xylonolactone.*—Trimethyl  $\gamma$ -xylose (1.5 g.) was dissolved in 12 c.c. of water, and 1 c.c. of bromine added gradually with shaking. The solution was then heated for 6½ hours at 30–35°. After keeping in the cold for 60 hours, it slightly reduced Fehling's solution. A further ½ c.c. of bromine was accordingly added and the oxidation completed by again heating for 9 hours at 35–40° and keeping over-night at room temperature. Excess of bromine was then removed by aeration, and the solution concentrated under diminished pressure. Hydrobromic acid was removed by the usual treatment, and the solution evaporated at 40°. The residual syrup was dissolved in dry ether and filtered several times

to remove traces of inorganic matter. In this way, 1.3 g. of a pale yellow liquid were obtained, which was submitted to fractionation in a high vacuum. Nearly the whole distilled at about  $105^{\circ}/0.04$  mm., and showed  $n_D$  1.4465 (Found: C, 50.7; H, 7.6; OMe, 47.4. Calc. for  $C_8H_{14}O_5$ , C, 50.5; H, 7.4; OMe, 48.9%).

On titration, the compound behaved as a lactone: 0.1060 g. required, on heating, 5.4 c.c. of  $N/10$ -sodium hydroxide (Calc. for  $C_8H_{14}O_5$ , 5.6 c.c.). The compound behaved in aqueous solution as a typical  $\gamma$ -lactone; there was a slow change in the value of the specific rotation due to the opening of the lactone ring, with formation of an acid of lower rotatory power. The following rotations were observed in aqueous solution ( $c = 1.1062$ ):  $[\alpha]_D + 74.1^{\circ}$  after 5 minutes,  $71.8^{\circ}$  after 64 hours,  $69.6^{\circ}$  after 7 days,  $61.4^{\circ}$  after 21 days.

The experimental evidence stated above has led to the conclusion that the oxidation product was trimethoxy- $\gamma$ -xylonolactone, and a 1:4 or butylene-oxide structure has thus been assigned to the derivatives of  $\gamma$ -xylose.

*Preparation of Trimethyl  $\delta$ -Xylonolactone from the Normal Form of Trimethyl Methylxyloside.*—A simultaneous hydrolysis and oxidation of crystalline trimethyl  $\beta$ -methylxyloside (m. p.  $48-49^{\circ}$ ) was carried out as follows (compare Pryde, Hirst, and Humphries, J., 1925, 127, 348): A solution of the normal form of the xyloside (1.5 g.) in 16.6 c.c. of 3% aqueous hydrobromic acid was heated at  $85^{\circ}$  for an hour and cooled to  $75^{\circ}$ . Bromine was then added (0.7 c.c.) over a period of 4 hours at the rate of 7 drops every half-hour. The solution stood at room temperature for 24 hours and then a further 1 c.c. of bromine was added at  $75^{\circ}$  over a period of 4 hours at the rate of 10 drops every half-hour. The liquid still reduced Fehling's solution after cooling and keeping over-night. More bromine (0.5 c.c.) was introduced over a period of 6 hours at the same temperature as before. On keeping over-night, the oxidation was found to be complete, and the product was isolated in the usual way. The yellow liquid thus obtained (1.13 g.) crystallised on the addition of ether. It was considered advisable, however, to distil the product in order to decompose any free acid that might be present. The product having been heated on a bath at  $100-110^{\circ}/0.05$  mm. for  $1\frac{1}{2}$  hours, the bath temperature was raised to  $145-150^{\circ}$ ; the product then distilled smoothly at  $115-120^{\circ}/0.05$  mm. as a colourless liquid which solidified, and the crystalline mass was drained on porous tile (m. p.  $52-53^{\circ}$ ). It recrystallised from light petroleum (sparingly soluble) in very long needles melting sharply at  $55^{\circ}$ . A further recrystallisation produced no change in the melting point. The recrystallised material resembled glass wool in appearance,



and analysis proved it to be trimethoxyxylonolactone, which must be the  $\delta$ -lactone, since the normal trimethyl xylose gives rise on oxidation to trimethoxyglutaric acid (Hirst and Purves, *loc. cit.*) (Found: C, 50.8; H, 7.5; OMe, 48.9. Calc. for  $C_8H_{14}O_5$ , C, 50.5; H, 7.4; OMe, 48.9%). On titration the compound behaved as a lactone: 0.1025 g. required, on heating, 5.15 c.c. of  $N/10$ -sodium hydroxide (Calc. for  $C_8H_{14}O_5$ , 5.39 c.c.). The hydrolysis of the lactone in aqueous solution at room temperature ( $c = 1.3289$ ) was followed polarimetrically:  $[\alpha]_D^{25} - 3.8^\circ$  after 4 minutes,  $+ 2.3^\circ$  after  $1\frac{1}{2}$  hours,  $+ 3.0^\circ$  4 hrs.,  $+ 6.9^\circ$  23 hrs.,  $+ 15.8^\circ$  4 days,  $+ 19.5^\circ$  6 days,  $+ 20.8^\circ$  8 days.

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## CXXII.—*Termolecular Reactions. Reduction of Silver Acetate by Sodium Formate.*

By ALEXANDER COUTIE.

IN a recent investigation of the reaction occurring between formaldehyde and bases, the author had occasion to make use of various velocity equations, in an attempt to settle the order of reaction. A comparison of the formulæ employed by other experimenters, working along similar lines, showed that in many cases these were in error. This can best be explained by reference to the fundamental differential equation, which is readily arrived at in the following way.

Multimolecular chemical reactions are of two types. The first class consists of those in which the participation of one molecule of each of  $n$  different substances, all originally of the same molar concentration, is necessary and sufficient for the occurrence of the change. The differential equation assumes the form

$$-dC/dt = kC^n \quad (1)$$

(All concentrations in this section may be taken as measured in g.-mols. per litre.) The other class is much more general, and includes those reactions in which the  $n$  molecules, taking part in the change, are not all different. If  $m_1$  molecules of substance A,

reacting with initial concentration  $C_1$ , disappear for every  $m_2$  molecules of substance B—of original concentration  $C_2$ —and so on

$$-dC/dt = kC_1^{m_1}C_2^{m_2}C_3^{m_3} \dots \quad (2)$$

where  $m_1 + m_2 + m_3 + \dots = n$ .

This equation can be put in a more useful form. If several substances A, B, C, . . . , with initial concentrations  $a, b, c, \dots$ , take part in a simple reaction, undisturbed by any simultaneous or secondary changes, and if  $l, m, n, \dots$  are the numbers of molecules of A, B, C, . . . which must react simultaneously before the change considered can take place, then, when  $x$  is the actual fall in concentration, in time  $t$ , of a substance of which only one molecule is necessary for the progress of the reaction,

$$dx/dt = k(a - lx)^l (b - mx)^m (c - nx)^n \dots \quad (3)$$

the number of factors being equal to the number of different substances taking part in the reaction. A similar equation has been given by Wegscheider (*Z. physikal. Chem.*, 1900, 35, 513).

From this general equation can be deduced all the ordinary unimolecular, bimolecular, etc., velocity formulæ, but in certain cases it leads to forms at variance with those already mentioned as being employed by a number of investigators. The disputed equations refer to reactions in which two or more molecules of at least one of the substances present are necessary for the progress of the change, i.e., when one or more of the quantities  $l, m, n, \dots$  in equation (3) is greater than unity. Applied to termolecular reactions of this type, as being those with which the author was chiefly concerned, the general equation gives the following formulæ.

*Termolecular.*—When a change takes place involving the interaction of three molecules of A, the sole reactant present, equation (3) reduces to

$$dx/dt = k(a - 3x)^3 \quad (4)$$

but when two molecular species A and B take part—their initial concentrations being  $a$  and  $b$ , respectively—and two molecules of B react with one of A, then

$$dx/dt = k(a - x)(b - 2x)^2 \quad (5)$$

In a formula such as (4)—where  $a$  is the total initial concentration of the reactant of which three molecules take part in the change, and  $x$  is the reduction in concentration, in time  $t$ , due to *each* molecule reacting—it is quite allowable, if absolute values of the velocity coefficient are not required, to make the substitution  $x_1 = 3x$ , whence

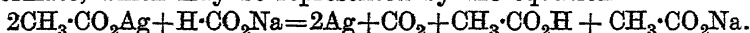
$$[dx_1/dt = k_1(a - x_1)^3 \quad (6)$$

and  $k_1 = 3k$ . It is obviously not justifiable to make such a substitution in one term of a differential equation and not in another. For example, the values of  $k$  obtained from equation (5) are not constant multiples of those derived from the form

$$dx/dt = k(a - x)(b - x)^2 \quad (7)$$

It is in this virtual neglect of the coefficients of  $x$  that the experimenters already referred to were in error.

For instance, Noyes and Cottle (*Z. physikal. Chem.*, 1898, 27, 579; *J. Amer. Chem. Soc.*, 1899, 21, 250) employ formula (7) in their study of the reaction between silver acetate and sodium formate, which may be represented by the equation



They state that in this formula  $a$  and  $b$  are the initial concentrations of sodium formate and silver acetate, respectively, and  $x$  the measured fall in concentration of the latter substance. Although the concentration of the silver acetate falls at twice the rate of that of the sodium formate, their formula does not show this. Moreover, their formula is restricted in its application when  $a$  is less than  $b$ , in which case it can only be employed as long as  $x$  is less than  $a$ , i.e., during the first half of an experiment. Noyes and Cottle continued their work past the point of half-decomposition in all experiments except, unfortunately, those to which this applies. The formula which they should have used is evidently

$$dx/dt = k(a - x/2)(b - x)^2 \quad (8)$$

This is identical in form with equation (5).

The use of erroneous formulæ of the above type by several workers is possibly due to their having accepted without question or appropriate modification those given by Ostwald ("*Lehrbuch der allgemeinen Chemie*," 1887, II, 615—634) and integrated by Fuhrmann (*Z. physikal. Chem.*, 1889, 4, 89), which are all of a simple and straightforward nature.

#### *Reduction of Silver Acetate by Sodium Formate.*

Since the days of van 't Hoff it has been recognised that reactions of order higher than the second are few in number, and certain examples brought forward from time to time have been severely criticised and shown to afford little or no evidence in favour of such changes. A reaction frequently quoted as being one of the most thoroughly investigated and typical examples of a termolecular transformation, and one which has never been seriously called in question, is that under discussion.

In their investigation of this reaction Noyes and Cottle (*loc. cit.*)

obtained velocity coefficients by the use of an erroneous formula (compare previous page).

Substitution of their data in the correct equation gives values which are far from constant, as can be seen from the following example.

$$a = [\text{H}\cdot\text{CO}_2\text{Na}] = 0.050 \text{ N}; \quad b = [\text{CH}_3\cdot\text{CO}_2\text{Ag}] = 0.100 \text{ N}.$$

<i>t</i> (mins.).	<i>b</i> - <i>x</i> .	<i>k</i> <sub>2</sub> (Noyes and Cottle).	<i>k</i> <sub>2</sub> (corrected).
2	0.08103	30.0	26.2
4	0.07180	30.2	23.5
7	0.06395	21.2	20.6
11	0.05920	29.7	16.9
16	0.05625	28.0	13.5

These facts suggested inaccuracy in their experimental work, which, although correct in outline, may be criticised on one or two points.

To begin with a matter of minor importance, the temperature at which they carried out their experiments was the boiling point of water under the atmospheric pressure, and although, owing to the short duration of a single experiment, the error thus introduced would not be appreciable except in the comparison of the velocity coefficients of the various experiments, yet an ordinary change in pressure might result in an error of 10% in the coefficients.

Whilst excessively slow reactions cannot be relied on to give satisfactory results, it must also be recognised that very quick reactions are subject to great experimental error. There was no need for these investigators to perform their experiments at 100°, with consequent times of half-decomposition of the order of a few minutes; a temperature of 75° gives a velocity at once convenient from the point of view of the time required and capable of accurate measurement.

The method of titration employed by Noyes and Cottle is liable to slight inaccuracy on account of difficulties in the quantitative filtration of the finely-divided suspension resulting from the addition of the reaction mixture to the thiocyanate solution. The author considers that the error thus introduced may account, at least in part, for the apparently abnormal data obtained by these investigators.

It need scarcely be emphasised that their experiments afford absolutely no proof that the reaction is of the third order.

#### *Re-investigation of the Reaction.*

The procedure was as follows. Solutions of the two salts at the same temperature ( $74.97^\circ \pm 0.02^\circ$ ) were rapidly mixed in such proportions that the resulting solution was of a known concentration with regard to each. One solution was placed in a boiling tube,

*A*, which was fitted with a syphon tube, leading to the bottom of a similar vessel, *B*, containing the other solution, and also with an inlet tube through which air could be passed to force the liquid from *A* into *B*. The apparatus was standardised in order to allow for the small quantity of solution unavoidably remaining in vessel *A* and in the syphon tube. At a definite time after the two had been mixed and thoroughly agitated by a current of air, an analysis sample of about 10 c.c. was withdrawn, and rapidly cooled in ice. As it was essential to remove the insoluble products of reduction before titration, a very small filter-paper was well washed with 2 c.c. of the cooled solution and the remainder was filtered through it. Attention to the size of paper and the preliminary washing was necessary to reduce the loss due to adsorption of silver salt during filtration. 5 C.c. of the filtered solution were titrated with potassium thiocyanate, ferric alum being used as indicator, the accuracy being 0.02 c.c. Consideration was given to various possible sources of error, such as the colloidal products of reduction not retained by the filter and dissolved by the nitric acid in the indicator solution, and the change in normality of the solutions on heating to 75°.

Silver acetate and sodium formate give alkaline solutions, and as the change to an acid reaction, which takes place during the course of an experiment, might have introduced disturbances, experiments were performed in which varying amounts of acetic acid were added initially. Since the results with and without acid were sensibly the same, this precaution was not considered essential.

The tables of results give the velocity coefficients calculated from the correct formula in the column headed *k* (correct), and, for comparison, those obtained by the use of Noyes and Cottle's formula under the heading *k*(N. and C.). The correct formula,  $\frac{dx}{dt} = k(a - x/2)(b - x)^2$ , where *a* and *b* are the total initial normalities of sodium formate and silver acetate, respectively, and *x* is the fall in normality of silver acetate in time *t*, gives on integration

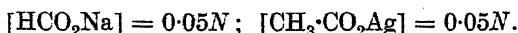
$$k = \frac{2}{(2a - b)^2 t} \left\{ \frac{(2a - b)x}{b(b - x)} + \log_e \frac{2a(b - x)}{b(2a - x)} \right\},$$

while Noyes and Cottle's equation  $\frac{dx}{dt} = k(a - x)(b - x)^2$ , where *a*, *b* and *x* have the same significance as above, gives

$$k = \frac{1}{(a - b)^2 t} \left\{ \frac{(a - b)x}{b(b - x)} + \log_e \frac{a(b - x)}{b(a - x)} \right\}.$$

The values of *x* given are calculated from the mean titration figures of from three to six experiments for each concentration. The accuracy obtained can best be shown by comparing the figures

for a single concentration:  $t$  is the time in minutes,  $s$  the values (c.c.) from a single experiment, and  $r$  the average of three experiments.



$t$ .....	20	40	70	100	160	240
$s$ .....	8.98	7.19	5.58	4.55	3.28	2.37
$r$ .....	8.97	7.19	5.59	4.56	3.28	2.41

### Tables of Results.

$$a = 0.100; b = 0.050.$$

$t$ (mins.).	$x$ .	$k$ (corr.).	$k$ (N. and C.).	$t$ (mins.).	$x$ .	$k$ (corr.).	$k$ (N. and C.).
20	0.0218	8.28	8.92	100	0.0395	8.84	10.81
40	0.0299	8.26	9.32	160	0.0433	9.79	12.55
60	0.0344	8.36	9.75	240	0.0460	11.94	15.98

The initial concentrations and the ranges of  $k$  (corr.) and  $k$  (N. and C.) in three similar experiments were:

$a = 0.050,$	$b = 0.050,$	$k$ (corr.) = 8.45—10.25,	$k$ (N. and C.) = 9.40—21.77
0.050,	0.025,	9.49—11.46,	9.75—13.73
0.025,	0.050,	8.61—9.48,	9.64—32.52*

\* These figures refer only to the first half of the reaction, as Noyes and Cottle's formula cannot be applied after the point of half-decomposition (compare p. 889).

Values calculated from the bimolecular formula are in all cases far from constant.

The following table gives the velocity coefficients, calculated from the correct formula, corresponding to the times of half-decomposition.

$a$ .....	0.100	0.050	0.050	0.025
$b$ .....	0.050	0.050	0.025	0.050
$k$ .....	8.3	8.5	9.7	9.4

These figures indicate that, whilst the reduction of a silver salt in dilute solution by a formate is not a rigid termolecular reaction, yet, both from the point of view of the constancy of the values in any one experiment and from the slight variation in the magnitude of the constant with change in initial concentration of the reactants, it appears that the reaction is essentially one of the third order.

### Summary.

The correct velocity equation has been deduced for those termolecular reactions in which two molecules of one of the reactants take part in the change.

Definite proof has been advanced that the reduction of silver acetate by sodium formate is essentially a reaction of the third order.

The author wishes to express his indebtedness to Professor Sir James Walker for the interest he has taken in this work and for much helpful criticism and advice.

UNIVERSITY OF EDINBURGH.

[Received, January 27th, 1926.]

### CXXIII.—*The Relative Concentrations of Various Electrolytes required to salt out Soap Solutions.*

By JAMES WILLIAM MCBAIN and ALBERT VINCENT PITZER.

IN a series of papers from this laboratory on the soap-boiling processes, it has been shown that there is a remarkable family likeness between the various soaps, whether pure, mixed or commercial, and that they differ in degree rather than in kind (McBain and Burnett, J., 1922, 121, 1320; McBain and Langdon, J., 1925, 127, 852; McBain and Elford, this vol., p. 421; McBain and Walls, *Fourth Report on Colloid Chemistry of the Brit. Asscn. for the Advancement of Science*, 1922, 244; McBain, Chap. in Vol. I of J. Alexander's forthcoming treatise on Colloids).

It has been shown that the phase-rule equilibria for each soap or mixture of soaps are affected in the same way by various salts; so that numerical ratios exist between the concentrations of individual salts required to produce the same effect upon any soap. Further, the effects in a mixture of electrolytes are additive. Likewise, the behaviour of a mixture of soaps seems to be approximately that expected from their respective constituents, apart from formation of curd or crystals.

Hence in order to be able to predict the concentration of any salt, or mixture of salts, required to obtain a specified equilibrium in any soap or mixture of soaps, two things are necessary. First, sufficient points must be established for the phase-rule diagram of each pure soap, using any one salt. Second, the numerical ratios between the concentrations of various salts required to produce a given salting out must be established with one concentration of any one soap. It is the object of the present communication to obtain the numerical ratios between various salts, using in every case 0.25*N*<sub>∞</sub> (weight normal)-sodium palmitate and making the definite comparison at 90°.

#### EXPERIMENTAL.

The method used has been sufficiently described in the papers previously mentioned. It depends on the separation of two isotropic liquid layers from one homogeneous liquid on gradual cooling from high temperatures.

0.25 $N_w$ -Sodium palmitate solutions were sealed up in strong glass tubes with various weights of specimens of the purest salts obtainable, and heated (in many cases far above the boiling point) until the contents of the tube were seen to be clear and perfectly homogeneous. They were then cooled slowly in a bath of glycerol until separation occurred. The experiments were carried out at different times during the past 5 years by C. S. Adams, L. S. Staddon, and the authors, with different samples of sodium palmitate, but the whole work was repeated this year by one of us (A. V. P.), using three different specimens of soap.

The results are in the following tables, all the qualitative observations of appearance, etc., being suppressed for lack of space.

Concentrations are given in every case in weight normality ( $N_w$ ) defined here as g.-mols. (not equivalents) per 1000 g. of water. The data are also given in g. per 100 g. of total system.

Table I gives results obtained with a sample (a) of ordinary sodium palmitate obtained from Messrs. Kahlbaum in March, 1925. It was shown to be the sodium salt of a mixture of fatty acids of mean molecular weight about half-way between palmitic and stearic.

Table II gives results obtained with a sample (b) of pure sodium palmitate specially prepared by Messrs. Kahlbaum in September, 1925. Analysis showed it to contain 0.0081 equivalent excess alkali per mol.

Table III gives results (c) obtained by making up the systems with palmitic acid "Kahlbaum" and sodium hydroxide solutions, by the method of Bunbury and Martin (J., 1914, 105, 417).

Table IV compares the concentrations of the various salts in mols. and in % by weight required to salt out at 90°, sodium chloride being taken as standard=1.00.

TABLE I.

*Minimum concentrations of various salts required to salt out solutions of 0.25 $N_w$ -sodium palmitate. March sample (a)—impure.*

*Sodium hydroxide.*

$N$ ...	0.933	1.10	1.10	1.11	1.17	1.30
Temp.	—	87	87.1	90	105.5	131.2°

*Sodium nitrate.*

$N_w$ ...	0.951	1.02	1.199	1.336
Temp.	80.7	108	151.8	173.6°

*Sodium chloride.*

$N_w$ ...	0.873	0.913	0.915	0.942	0.985	1.004	1.098	1.099	1.253
Temp.	80.3	97.5	111	119.7	128.5	134.2	156.9	157.5	178.1°

*Sodium acetate.*

$N_w$ ...	0.796	0.839	0.872	0.895	0.992	1.0471	1.12	1.23
Temp.	83	93	96.8	101	124.5	135.2	146	158°



TABLE II.

*Minimum concentrations of various salts required to salt out solutions of 0.25N<sub>w</sub>-sodium palmitate. September sample (b)—pure.*

<i>Sodium hydroxide.</i>									
N <sub>w</sub> ...	0.994	1.130	1.214	1.303	1.337				
Temp.	—	91.7	108	129.3	138°				
<i>Sodium nitrate.</i>									
N <sub>w</sub> ...	1.05	1.110	1.22	1.302					
Temp.	87	114	148.9	164.3°					
<i>Sodium chloride.</i>									
N <sub>w</sub> ...	0.955	0.971	0.999	1.110	1.199				
Temp.	89.6	98.5	105.5	135.3	157°				
<i>Sodium iodide.*</i>									
N <sub>w</sub> ...	0.802	0.844	0.872	0.887	0.905	0.987			
Temp.	67.4	70.4	74.2	75.5	89.5	106.5°			
<i>Sodium bromide.</i>									
N <sub>w</sub> ...	0.865	0.895	0.920	0.955	0.966	0.986	0.982	1.109	1.20
Temp.	77	92	93	109.3	111.5	118	120.4	154.5	172°
<i>Sodium acetate.</i>									
N <sub>w</sub> ...	0.821	0.900	0.966	1.00	1.063	1.128	1.305		
Temp.	75	91.7	102.5	108	123	133	154°		
<i>Sodium carbonate.</i>									
N <sub>w</sub> ...	0.887	0.897	0.933	0.953	0.983	0.995	1.064	1.064	1.107
Temp.	90	91	106.7	110.8	118	120.3	136	137.6	143
N <sub>w</sub> ...	1.157	1.211							
Temp.	153	159.6°							
<i>Sodium sulphate.</i>									
N <sub>w</sub> ...	0.826	0.904	0.963	0.997	1.074	1.11	1.18		
Temp.	90	103.5	119.7	134	147.5	151.6	164.5°		
<i>Sodium tungstate.</i>									
N <sub>w</sub> ...	0.651	0.700	0.738	0.801					
Temp.	93.8	114.4	132	153°					
<i>Sodium tartrate.</i>									
N <sub>w</sub> ...	0.634	0.676	0.699	0.757	0.778	0.790	0.903		
Temp.	85	104.5	115	137.2	141	151.5	176°		

\* A different sample of sodium palmitate was used in this case.

TABLE III.

*Minimum concentrations of various salts required to salt out solutions of 0.25N<sub>w</sub>-sodium palmitate. Pure samples (c) prepared from palmitic acid "Kahlbaum" and sodium hydroxide solution.*

<i>Sodium hydroxide.</i>									
N <sub>w</sub> ...	1.097	1.127	1.253	1.341					
Temp.	86.3	97.3	121	138.4°					
<i>Sodium chloride.</i>									
N <sub>w</sub> ...	0.965	1.00	1.017	1.044	1.116	1.199			
Temp.	92.6	105.5	114	120	140.7	161°			
<i>Sodium thiocyanate.</i>									
N <sub>w</sub> ...	0.757	0.814	0.950	1.027					
Temp.	86	110.5	146	173.3°					

TABLE IV.

*Minimum concentrations of various electrolytes (hydroxide and salts of sodium) required to salt out  $0.25N_w$  solutions of sodium palmitate at  $90^\circ$  (sodium chloride = 1.00).*

Electrolyte.*	Mol. wt.	Concn. reqd.		Ratio.	
		$N_w$	% by wt.	$N_w : N_w$	% : %
Hydroxide .....	40.01	(1.110) (a)	3.99	1.24	0.86
		1.127 (b)	4.05	1.18	0.82
		1.106 (c)	3.97	1.16	0.80
		Mean		1.19	Mean 0.83
Nitrate .....	85.01	(0.970) (a)	7.16	1.08	1.54
		1.056 (b)	7.74	1.11	1.56
		Mean		1.10	Mean 1.55
Chloride .....	58.45	(0.895) (a)	4.66	1.00	1.00
		0.953 (b)	4.95	1.00	1.00
		0.955 (c)	4.96	1.00	1.00
		Mean		1.00	Mean 1.00
Iodide .....	149.9	0.905 (d)	11.27	0.95	2.19
Bromide .....	102.9	0.898 (b)	7.95	0.94	1.61
Acetate .....	82.02	(0.838) (a)	6.03	0.94	1.30
		0.895 (b)	6.42	0.94	1.30
		Mean		0.94	Mean 1.30
Carbonate .....	106.0	0.887 (b)	8.08	0.93	1.63
Sulphate .....	142.1	0.826 (b)	9.89	0.87	2.00
Thiocyanate .....	81.07	0.763 (c)	5.46	0.80	1.10
Tungstate .....	294	0.645 (b)	15.1	0.68	3.04
Tartrate .....	194.3	0.645 (b)	10.46	0.68	3.12

(a) = March sample of sodium palmitate (impure).

(b) = September sample of sodium palmitate (pure).

(c) = Sodium palmitate prepared from palmitic acid "Kahlbaum" and sodium hydroxide.

\* Sodium fluoride also was tested, but it was not sufficiently soluble to salt out the palmitate at  $90^\circ$ .

The electrolytes used, with the exception of sodium thiocyanate, were dried by heating at  $120$ — $130^\circ$ . The sodium thiocyanate was dried to constant weight in a vacuum over calcium chloride at room temperature.

All our numerical results are summarised in Table IV, showing the absolute and relative amounts of the various electrolytes required to salt out sodium palmitate at  $90^\circ$ .

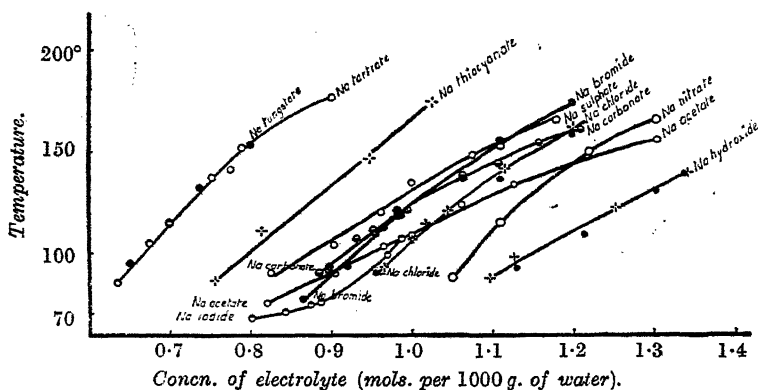
The only published data of sufficient accuracy by which to check our results are those from the Karlsruhe laboratory, which are based upon ratios obtained by Richert (*Dissert.*, Karlsruhe, 1911) for carbonate and hydroxide. He found, for various soaps, that 1.01 mols. of carbonate and 1.27 equivalents of hydroxide had the same effect as 1 equivalent of sodium chloride, whereas we have found 0.93 and 1.19, respectively. The divergence from our results amounts to about 6%.

To show the effect of temperature upon the various electrolytes the results have been plotted in Fig. 1. The figure shows that the ratios are not quite constant and independent of temperature, although the deviation does not exceed about 6%. This gives a second measure of the extent to which these data are generally valid, and they are borne out by an analysis of our unpublished data on commercial oils and fats as well as other results from the Karlsruhe laboratory and also the well-known data of Merklen.

An immense amount of information can be derived from these approximate numerical ratios which enables prediction to be made, well within 10%, of the maximum concentration of salts which

FIG. 1.

*Concentrations of electrolytes required to salt out 0.25N<sub>w</sub>-sodium palmitate.*



*(The crosses indicate results obtained with solutions made up from palmitic acid "Kahlbaum.")*

may be added to any soap solution without salting it out. They enable all the complicated mixtures used in commercial soap boiling to be reduced to a common basis for comparison and control. Taken in conjunction with the equilibrium diagrams now becoming available for pure and commercial soaps, whether derived from sodium or potassium, they facilitate the approximate prediction of the concentration of any mixture of electrolytes required to produce a given effect.

Perhaps the most unexpected feature of Table IV is that, as a first approximation, the salts do not replace each other equivalent for equivalent, but rather mol. for mol. irrespective of their valency. For example, sodium thiocyanate comes, in this respect, between sodium sulphate and sodium tungstate; and one mol. of sodium carbonate exactly replaces one equivalent of acetate or iodide.

The results here discussed bear no relation whatsoever to the

Hoffmeister series, as may be seen from the order of the electrolytes in Table IV. Equally, the results are at variance with what might have been expected from the equation of the Donnan equilibrium, since here the order of the electrolytes is irrespective of their valency.

The most comparable factor common to all the salts seems to be the concentration of the sodium ion. Although no data are available for the actual mixtures in the soap solutions, yet this point may be brought out from an examination of such conductivity data for aqueous solutions of pure electrolytes as are given in Landolt-Börnstein-Roth's "Tabellen." The concentration of the sodium ion for all the electrolytes except the acetate, thiocyanate, carbonate, tartrate, and hydroxide is almost exactly two-thirds normal, whereas for these five cases it is  $0.5N_w$ ,  $0.54N_w$ ,  $0.58N_w$ ,  $0.76N_w$ , and  $0.8N_w$ , respectively. It is clear, therefore, that the equilibria are not exclusively determined by the degree of dissociation into sodium ion, although this is predominant. Matters are not improved by an attempt to substitute for concentration of sodium ion, its activity. The data are available for the chloride and hydroxide and the activities are proportional to the total concentrations required to produce the same effect, whereas they should have been inversely proportional, thus revealing a discrepancy of about 40%.

#### *Summary.*

1. Measurements have been made of the relative salting-out action of eleven different electrolytes on soap solutions.

2. With the aid of numerical ratios derived therefrom it is possible to compare, predict, and control all the various equilibria obtained with pure and commercial soaps with any mixture of electrolytes to within an accuracy of about 5 to 10%.

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[Received, January 25th, 1926.]

### CXXIV.—*Hydrofluozirconic Acid and the Analysis of Zirconium Fluoride.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and EDWIN CLAXTON ROPER.

THIS investigation was undertaken with the object of verifying, or disproving, the existence of an acid fluoride of zirconium, or a hydrofluozirconic acid. Preliminary work on the ordinary hydrated fluoride led to results which do not altogether agree with those previously recorded. These previous results, so far as they are

relevant, may be summarised as follows. The evaporation of a solution of zirconium dioxide in hydrofluoric acid yields triclinic tablets, which, when dried to constant weight in air, consist of the trihydrate,  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$  (Chauvenet, *Compt. rend.*, 1917, **164**, 727). This compound begins to be dehydrated at  $100^\circ$ ; at  $140^\circ$  it loses 2 mols. of hydrogen fluoride, giving the dihydrate  $\text{ZrOF}_2 \cdot 2\text{H}_2\text{O}$ , and above  $140^\circ$  it becomes converted into  $\text{ZrOF}_2$ . In the cold, this absorbs hydrogen fluoride, giving the monohydrate or  $\text{ZrOF}_2 \cdot 2\text{HF}$ . A solution of the latter in water slowly deposits a substance which, when dried to constant weight, has the composition  $\text{ZrOF}_2 \cdot 2\text{H}_2\text{O}$ , and at  $120^\circ$  is converted into  $\text{ZrOF}_2$ .

Our experience supplements, and leads us to criticise, these results. Evaporation of solutions containing fluorides of zirconium yields only powders of indefinite composition, unless the evaporation is carried out at the ordinary temperature and under reduced pressure. The large crystals thus obtained cannot be dried in air to constant weight without decomposition of the surface layer, since they continually give off hydrogen fluoride. They must therefore be dried quickly and kept enclosed in waxed tubes. Compounds intermediate between the trihydrate and the oxyfluoride may exist, but the isolation of these would require a careful study of the partial pressures of hydrofluoric acid and water. Compounds of constant composition are not likely to be isolated simply by drying or heating to constant weight in contact with the atmosphere. The oxyfluoride is not obtained by heating the trihydrate in air above  $140^\circ$  for any reasonable time; the weight may become constant, but is greater than is required for this compound (*vide infra*). Further, it cannot be considered that the composition of any of these compounds is established by means of the zirconia content alone. There is no evidence in the work of Chauvenet (*loc. cit.*) that any analysis has been attempted beyond the obvious and comparatively easy estimation of zirconia. We have found that none of the methods of estimating hydrogen fluoride was satisfactory in the presence of dissolved zirconium compounds. It has been necessary to devise a new method, which was first tested with potassium hydrogen fluoride and then applied to the best authenticated compound,  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ . This compound, crystallised under the conditions mentioned above, appears as transparent or translucent, polygonal plates, the sides of which contain characteristic angles,  $109^\circ$ ,  $113^\circ$ ,  $121^\circ$ ,  $126^\circ \pm 1^\circ$ .

*Analysis.*—The calcination of this compound to oxyfluoride, with subsequent ignition to dioxide, requires some care, since a part may sublime, if it is heated too rapidly, either as the oxyfluoride or the tetrafluoride. After being gently heated in a covered crucible,

it was converted into the sulphate and then ignited to constant weight. Freshly-prepared crystals gave, as the mean of five analyses, 36.3% Zr, the extreme values being 34.4 and 38.0%. They thus appear to be more highly hydrated than the trihydrate, which requires 41.0%, or even than the tetrahydrate, which would require 38.0% Zr. Later preparations agreed more closely with the composition of the trihydrate. The necessity for determining another constituent was evident, and an apparatus was constructed in which the hydrogen fluoride could be volatilised. This consisted of a copper tube having an internal diameter of about  $\frac{1}{2}$  inch, which was cut with a special reamer and ground to fit a conical platinum stopper. This was continued as a platinum delivery tube which dipped in standard alkali. The platinum boat containing the compound to be analysed was placed in the copper tube close to, and partly entering, the platinum stopper. A current of dry air, or, in later experiments, superheated steam, was passed through the tube. The hydrofluoric acid evolved was absorbed in the alkali without loss, as was proved by analyses of potassium hydrogen fluoride.

*Results of Analysis.*—Samples A and B were prepared at different times but had the same composition. The rest were all taken from one preparation. A was first heated in air, the rest in steam. The relatively small amount of hydrogen fluoride which can be obtained by heating in air is noteworthy. The manner in which hydrolysis proceeds during the heating was determined by weighing the residues and titrating the hydrofluoric acid at various stages. When the compound was heated in dry air it lost hydrogen fluoride, which was formed by hydrolysis with the contained water, and also some of this water. The residue, when heated in undried air, lost no appreciable weight but gave off more hydrogen fluoride. In this case, more of the fluoride must have been hydrolysed, but by external water, some of which was retained :  $\text{ZrF}_4 + \text{H}_2\text{O} = \text{Zr}(\text{OH})\text{F}_3 + \text{HF}$ .

A portion of the residue was ignited to dioxide as described above. The hydrogen fluoride driven off by this operation may be calculated on the assumption that the compound is hydrolysed (a) by its own water, or (b) by external water. These two estimates, when added to the hydrofluoric acid titrated, furnish the two values in the last line of the table. The uncertainty arises from the fact that it is not possible, by the strongest heating which the apparatus permitted (between 300° and 400°) in a current of air, to drive off all combined hydrogen and to convert all the compound into  $\text{ZrOF}_2$ . The ratio of the weight of zirconia to that of the product heated in the tube was 0.77 instead of  $0.8473 = \text{ZrO}_2/\text{ZrOF}_2$ . When steam was used the hydrolysis was more complete. Sample C lost both hydrogen fluoride and water, the ratio of ignited zirconia to steam-

heated product being now 0.823. In the case of sample D, the ratio was 0.836. The percentages of hydrogen fluoride will accordingly be nearer to the higher value in the table. In order to obtain a direct titration of still more hydrofluoric acid, we arranged to hydrolyse at a higher temperature. A small platinum tube, closed at one end by a cap of platinum foil, was placed inside the platinum delivery tube, which was heated to bright redness in a current of superheated steam. Samples B and F were analysed by this method. Sample B yielded 34.0% of hydrogen fluoride when heated in steam below a red heat and a further 3.48% when heated to a bright red heat. The weight of the residue showed that it had been almost completely hydrolysed to oxide. In calculating the results, the quantities of zirconia and hydrogen fluoride were added together, and the water was obtained by difference.

	A.	B.	C.	D.	E.	F.
% $\text{ZrO}_2$ .....	58.8	57.6	53.9	54.0	(54)	(54)
% HF (titrated) .....	8.2	37.5	19.8	22.3	31.2	31.1
% HF total	25.7-	—	30.5-	32.9-	—	—
(estimated) .....	37.8	37.5	39	41.5	—	—

The weighted mean of the zirconia in A and B is 58.5, the hydrogen fluoride is 37.5, the water 4.0; the composition therefore corresponds to  $\text{ZrF}_4 \cdot 2.45\text{H}_2\text{O}$ . The preparation containing 54% of zirconia contains at least 31% of hydrogen fluoride in C and more than 33% in D. We estimate it at 35%, for the reason mentioned on previous page. The water will therefore be 11.0, corresponding to  $\text{ZrF}_4 \cdot 3.4\text{H}_2\text{O}$ . Thus the crystals do contain the tetrafluoride, but the water of crystallisation is proved to be variable.

*The Acid Fluoride.*—Numerous double fluorides have been prepared such as  $2\text{NH}_4\text{F} \cdot \text{ZrF}_4$ ;  $3\text{NH}_4\text{F} \cdot \text{ZrF}_4$ ;  $\text{KF} \cdot \text{ZrF}_4 \cdot \text{H}_2\text{O}$ ;  $2\text{KF} \cdot \text{ZrF}_4$  (Marignac, *Ann. Chim. Phys.*, 1860, 60, 271); also  $2\text{NaF} \cdot \text{ZrF}_4$  (Wells and Foote, *Amer. J. Sci.*, 1866, 3, 466). The salt  $2\text{KF} \cdot \text{ZrF}_4$  is one of the easiest to prepare, yet even in this case a slight excess of potassium fluoride produces  $3\text{KF} \cdot \text{ZrF}_4$ . The free acid might correspond to any of these salts. An acid salt is said to be deposited on rubbing the walls of a vessel containing a solution of zirconia in hydrofluoric acid (Fischer and Thiele, *Z. anorg. Chem.*, 1910, 67, 309). This dissolved readily in water, but with difficulty in concentrated hydrofluoric acid. When treated with lead carbonate, it gave a soluble lead salt which was believed to be  $\text{PbZrF}_6$ . Some soluble lead salt is certainly formed when lead carbonate is added to any solution containing zirconium fluoride, for, after removal of the lead fluoride by filtration, more lead may be precipitated from the filtrate by means of hydrogen sulphide, and the second filtrate contains both zirconium and fluorine.

A hydrofluozirconic acid is also said to be produced when hydrogen fluoride is absorbed by zirconium tetrafluoride (Chauvenet, *loc. cit.*). The isolation of an acid by either of these methods would appear to be difficult. We consider that the only method which offers any reasonable chance of success is to add much anhydrous hydrogen fluoride to a little zirconium fluoride which is already in solution.

*Preparation.*—The anhydrous acid, prepared by distilling dry sodium hydrogen fluoride in a copper still, was condensed in a platinum bottle or crucible which fitted into a copper receiver. After addition of this to the solution of zirconium fluoride or *vice versa*, a fine, white crystalline solid was usually deposited. This was cooled in a freezing mixture and well stirred. The liquid was then decanted, and the solid washed several times by decantation with dry ether and pressed on filter-paper. This substance has been prepared on five occasions. The appearance of the crystals was always the same, but very different from that of the ordinary fluoride. Under the microscope, they were seen to be of uniform type—long prisms with chisel-shaped ends. On exposure they gave off hydrogen fluoride and became dull on the surface. In a few days the whole crystal became opaque. When they were dissolved in a very little water (in which they are extremely soluble) and treated with a few drops of lead acetate, the liquid remained clear. A drop of hydrofluoric acid produced an immediate turbidity. The hydrofluozirconic acid was therefore not much hydrolysed.

*Analysis of the Acid Fluoride.*—One of the earlier samples, weighed rapidly in a closed platinum crucible with a tightly fitting lid and then converted into zirconia, contained 46.0%  $\text{ZrO}_2$ . In the case of the last sample, we were able to determine the hydrogen fluoride separately as described above, and to follow the course of the decomposition: (1) 0.4603 g. was heated in a current of dry air. The loss was 0.1359 g., of which 0.0772 g. was hydrogen fluoride. (2) The residue, 0.3244 g., was heated in steam. The loss was 0.0379 g., and the hydrogen fluoride 0.03619 g. This is the stage in which the hydrolysis proceeds at the expense of water of crystallisation. (3) A portion, 0.0863 g., of the last residue, when heated in steam to a bright red heat, lost 0.0196 g. The hydrogen fluoride was 0.01962 g. (4) Another portion, 0.0911 g., ignited with sulphuric acid, gave 0.0682 g. of dioxide. All quantities being referred to the original weight, the hydrogen fluoride lost in (3) is 0.0658 g., whilst the total loss in (4) is 0.0720 g. Since steaming at a red heat causes conversion nearly into  $\text{ZrO}_2$  with a little  $\text{ZrOF}_2$ , the final loss,  $0.0720 - 0.0658 = 0.0062$  g., represents hydrogen fluoride produced by the reaction  $\text{ZrOF}_2 + \text{H}_2\text{O} = \text{ZrO}_2 + 2\text{HF}$ , the water being derived from external sources such as the sulphuric acid. This loss must corre-



spond to a weight of hydrogen fluoride =  $40 \times 0.0062/22 = 0.0113$  g. The weight of zirconia calculated on the original weight of compound is 0.215 g., or 46.59%. On heating in dry air, 1 mol. of the compound loses rather more than 2 mols. of hydrogen fluoride and rather less than 2 mols. of water. On heating in steam, it loses rather more than 1 mol. of hydrogen fluoride, and, at a bright red heat, rather less than 2 mols. of the acid.

*Composition of the Acid.*—0.4603 G. gave 0.1792 g. HF (titrated) and 0.0113 g. (deduced from final loss of weight), total 0.1905 g.; and 0.0548 g. of  $H_2O$  (by difference). The simplest formula calculated from these results is  $ZrF_4 \cdot 1.5HF$ ,  $3.74H_2O$ , or  $ZrOF_2 \cdot 3.5HF$ ,  $2.74H_2O$ . On account of the difficulty in avoiding loss of hydrogen fluoride during the weighing, etc., and of the hygroscopic character of the compound, we consider that, as originally precipitated, it would probably contain the extra 0.5 mol. of hydrogen fluoride and 0.75 mol. less water, and that it would be hydrofluozirconic acid corresponding to the best known potassium salt, with the addition of about 3 mols. of water of crystallisation, i.e.,  $H_2ZrF_6 \cdot 3H_2O$ .

One of us (E. C. R.) desires to acknowledge the continuance of a maintenance grant from the Department of Scientific and Industrial Research which enabled this work to be completed. We also desire again to record our indebtedness to the Royal Society for a former grant towards the purchase of apparatus.

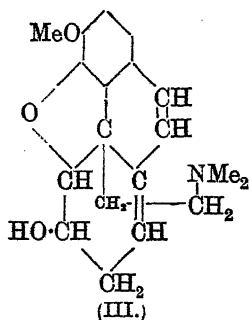
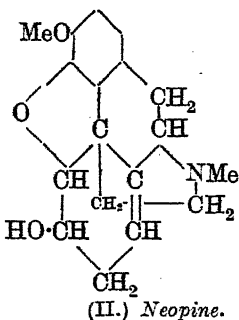
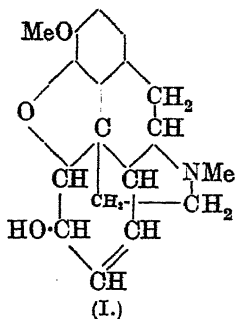
UNIVERSITY COLLEGE, NOTTINGHAM. [Received, December 14th. 1925.]

### CXXV.—*The Morphine Group. Part III. The Constitution of Neopine.*

By CONSTANT FREDERIK VAN DUIN, ROBERT ROBINSON, and  
JOHN CHARLES SMITH.

THE rare opium alkaloid which is the subject of this communication was discovered by Messrs. T. and H. Smith of Edinburgh in the final mother-liquors from the isolation of opium alkaloids and separated in the form of its readily crystallisable hydrobromide. Dobbie and Lauder (J., 1911, 99, 34) investigated this salt and the amorphous base which could be obtained from it and concluded that neopine is a hydroxycodine. We found that neopine hydrobromide, for a supply of which we are greatly indebted to Messrs. T. and H. Smith, possessed the properties described by Dobbie and Lauder. The analysis, however, gave the formula  $C_{13}H_{22}O_3NBr$  instead of  $C_{13}H_{22}O_4NBr$  required for a hydroxycodine hydro-

bromide. The free base was obtained in a crystalline condition, m. p. 127.5° (corr.), and was found to have the formula  $C_{18}H_{21}O_3N$ . It appeared to be an isomeride of codeine and this was confirmed by the examination of several derivatives. Moreover, like codeine, neopine contains one methoxyl group, one alcoholic hydroxyl group, and one methyl group attached to nitrogen. The close relation of the base to codeine is brought out in a very clear light by the fact that catalytic hydrogenation of neopine leads to the formation of dihydrocodeine. It will be recalled that the decomposition of codeine methohydroxide leads to the formation of  $\alpha$ -methylmorphimethine, which is changed to an isomeric  $\beta$ -methylmorphimethine by means of boiling alcoholic potassium hydroxide. The decomposition of neopine methohydroxide gives at once pure  $\beta$ -methylmorphimethine. Neopine is thus to be regarded as  $\beta$ -codeine; it stands to codeine in the same relationship that  $\beta$ -methylmorphimethine bears to  $\alpha$ -methylmorphimethine. In Parts I and II of this series (J., 1923, 123, 980, 998) Gulland and Robinson suggested a new formula for codeine, but they modified this expression in a subsequent paper\* (*Mem. Manchester Phil. Soc.*, 1925, 69, No. 10), in that they returned to the view that codeine is an unsaturated substance and put forward the formula (I) as the best representation of the constitution of the base. The corresponding expressions for neopine and  $\beta$ -methylmorphimethine (unchanged from Part I) are (II) and (III), respectively.



\* This paper was read at a meeting of the Manchester Literary and Philosophical Society on February 7th, 1925, and a statement of the proposed change in the morphine formula was given in an abstract in *Nature* (1925, 115, 625). The memoir could be purchased in a separate form in July, 1925. About the same time, Wieland and Kotake (*Annalen*, 1925, 444, 69) emphasised the unsaturated nature of codeine and located the double bond in the new position also adopted by Gulland and Robinson. The above particulars are contributed in order to prove that the suggestions of Gulland and Robinson and of Wieland and Kotake were independent and contemporaneous.

The existence of a  $\beta$ -codeine might be anticipated on the basis of many codeine formulæ, but it should be noted that neopine is less readily oxidised by permanganate and also less readily catalytically hydrogenated than codeine. Any hypothesis, therefore, of the relation of codeine to neopine or of  $\alpha$ - to  $\beta$ -methylnorphimethine which suggests that codeine has a bridge ring that becomes an ethylene linking in neopine is definitely opposed to the facts. The only possible conclusion that can be drawn from the circumstance that neopine is more stable than codeine towards reagents for the ethylene linking is that the latter contains a double bond which moves, in the transformation of  $\alpha$ -methylnorphimethine to the  $\beta$ -isomeride, to a more sheltered position or at least to a position in which it exhibits a smaller degree of reactivity.

#### EXPERIMENTAL.

*Neopine Hydrobromide.*—The substance provided by Messrs. T. and H. Smith was anhydrous and remarkably homogeneous. It darkened from about  $240^\circ$ , became very dark at  $279^\circ$ , blackened at  $281^\circ$ , and melted with decomposition at  $282$ – $283^\circ$  (Found: Br, by titration, 21.1.  $C_{18}H_{22}O_3NBr$  requires Br, 21.0%). The salt was dried at  $100^\circ$  for 5 hours (Found: Br, 21.1%); it was then recrystallised and dried at  $100^\circ$  for 5 hours (Found: Br, 21.1%). The identity of the material with that examined by Dobbie and Lauder (*loc. cit.*) is evident from the determination of the rotatory power. The salt supplied by Messrs. T. and H. Smith dried at  $100^\circ$  for 5 hours had  $[\alpha]_D^{25} + 17.08^\circ$  in aqueous solution ( $c = 5.152$ ). After recrystallisation and drying at  $100^\circ$ , we found  $[\alpha]_D^{25} + 17.32^\circ$  ( $c = 3.696$ ). Dobbie and Lauder found  $[\alpha]_D^{20} + 17.07^\circ$  ( $c = 5.1884$ ) and  $[\alpha]_D^{20} 17.4^\circ$  ( $c = 5.0741$ ).

*Neopine.*—The hydrobromide was dissolved in water, decomposed by the addition of sufficient concentrated aqueous potassium hydroxide to produce an emulsion (the base is rather readily soluble in water), and the neopine thrice extracted with benzene. The benzene solutions were dried with potassium carbonate and evaporated, leaving a soft varnish. This was dried at about  $80^\circ$  and after some hours a crystal nucleus was noticed. On cooling and scratching, the whole varnish crystallised and the crude product had m. p.  $125^\circ$ . The base is best recrystallised from light petroleum (b. p.  $80$ – $100^\circ$ ) and separates in long, glistening, brittle, colourless needles, m. p.  $127$ – $127.5^\circ$  (corr.) (Found in material heated at  $80^\circ$ : C, 72.4; H, 7.1; N, 4.6, 4.7\*, 4.7\*; MeO, 10.5\*, 10.4\*; NMe\*, 5.2;  $M$  in camphor, 288.  $C_{18}H_{21}O_3N$  requires C, 72.2; H, 7.0; N, 4.7; MeO, 10.4; NMe, 5.0%;  $M$ , 299).

\* By micro-methods.

In aqueous solution ( $c = 5.1084$ ) the base is apparently optically inactive ( $D$  line at  $20^\circ$ ), but on the addition of hydrochloric acid (Neop.,  $HCl$  in  $0.397N\text{-}HCl$ ) the value  $[\alpha]_D^{25} + 18.85^\circ$  was observed. In dry chloroform ( $c = 7.4740$ ), we found  $[\alpha]_D^{25} - 28.10^\circ$  for the base. With the Froehde and Mandelin reagent, codeine and neopine give yellow colorations changing to blue; this change appears to be slower in the case of neopine. The alkaloid dissolves in water, and a very dilute solution does not immediately decolorise a drop of dilute aqueous potassium permanganate which is added to it. Under similar conditions, codeine rapidly reduces the oxidising agent.

*Acetylneopine*.—A hydroxycodeine has the same state of oxidation as thebaine, and before we were aware of the true composition of neopine an attempt to degrade it was made under the conditions of the preparation of diacetylthebaol from thebaine, but the result was negative. Neopine (4 g.) was acetylated in 2 hours with boiling acetic anhydride (15 c.c.) in presence of anhydrous sodium acetate (2 g.), and the resulting solution added to water and rendered alkaline by means of sodium carbonate. The base, isolated by means of ether, was obtained as a pale yellow varnish which has not yet been crystallised [Found:  $CH_3\cdot CO$ , 12.7 (by A. G. Perkin's method; J., 1905, 87, 107).  $C_{18}H_{20}O_3N\cdot CO\cdot CH_3$  requires  $CH_3\cdot CO$ , 12.6%]. Acetylneopine combines very readily with methyl iodide in methyl-alcoholic solution; the product crystallises from methyl alcohol in long, glistening needles which probably contain solvent of crystallisation, since they lose their lustre on heating. *Acetylneopine methiodide* darkens at  $250^\circ$  and has m. p.  $256\text{--}257^\circ$  (decomp.; corr.) (Found in material dried at  $95\text{--}100^\circ$  to constant weight: C, 52.4; H, 5.5; I, by titration, 26.15.  $C_{21}H_{26}O_4NI$  requires C, 52.2; H, 5.4; I, 26.3%).

*Catalytic Hydrogenation of Neopine with Formation of Dihydrocodeine*.—The reductions were carried out at the ordinary temperature in a vessel filled with hydrogen and provided with a stirrer. Codeine (5 g.) dissolved in water (50 c.c.) and acetic acid (2 c.c.) absorbed in 25 minutes 385 c.c. of hydrogen in presence of colloidal palladium (from 10 c.c. of 0.5% palladous chloride\*). This was equivalent to 370 c.c. at *N.T.P.* The volume theoretically required for the saturation of one double bond is 375 c.c. The isolated product had at first m. p.  $55^\circ$  and was dried at  $110^\circ$ . It then melted at  $112\text{--}113^\circ$  (corr.) after crystallisation from water containing a few drops of methyl alcohol. This was the highest value that could be obtained. Skita and Frank (*Ber.*, 1911, 44, 2865) gave the m. p.

\* The solution employed in both reductions contained also 0.5% of gum arabic.

of dihydrocodeine as  $65^{\circ}$ , whilst Freund (*J. pr. Chem.*, 1920, **101**, 12) gave  $86-88^{\circ}$ . Oldenburg (D.R.-P. 260,233) also quoted the value  $62-63^{\circ}$ . Mannich and Löwenheim (*Arch. Pharm.*, 1920, **258**, 304) showed that dihydrocodeine with  $2\text{H}_2\text{O}$  melts at  $55^{\circ}$  or  $88^{\circ}$ , whilst the anhydrous substance has m. p.  $111-112^{\circ}$ . Wieland and Koralek (*Annalen*, 1923, **433**, 269) crystallised the base from 80% methyl alcohol, a process which we cannot repeat, and gave the m. p.  $112-114^{\circ}$ .

A solution of neopine (2.5 g.) in water (25 c.c.) and acetic acid (1 c.c.) containing colloidal palladium (5 c.c. of 0.5% palladous chloride) was stirred in hydrogen, when the palladium was at once flocculated. More palladous chloride solution (10 c.c.) was added, but flocculation again occurred. In about 15 hours, 180 c.c. of hydrogen were absorbed (equiv. to 176 c.c. at *N.T.P.*; calc., 185 c.c.). The base was rendered to chloroform from the filtered solution and, after removal of the solvent, the residual oil crystallised when inoculated with dihydrocodeine (variety, m. p.  $55^{\circ}$ ). This material melted at  $51-53^{\circ}$ , but after resolidification it had m. p.  $81-84^{\circ}$  and after drying at  $80^{\circ}$  for 1 hour the m. p. was  $110-111^{\circ}$ . After crystallisation from water containing a few drops of methyl alcohol, the substance dried at  $80^{\circ}$  had m. p.  $112-113^{\circ}$  (corr.) (Found: C, 71.5; H, 7.9. Calc. for  $\text{C}_{18}\text{H}_{23}\text{O}_3\text{N}$ : C, 71.7; H, 7.7%). Approximately equal quantities of dihydrocodeine, m. p.  $112-113^{\circ}$ , and dihydroneopine, m. p.  $112-113^{\circ}$ , were melted together on a watch glass. The mixture rapidly crystallised on cooling and had m. p.  $112-113^{\circ}$ .

*Conversion of Neopine into  $\beta$ -Methylmorphimethine.*—Neopine combined rapidly with methyl sulphate in benzene solution to a *methosulphate*, which separated in a resinous condition. It was very deliquescent and readily soluble in water and on the addition of potassium hydroxide to the solution no precipitation occurred. On boiling, the methine suddenly made its appearance as oily drops, and these crystallised at once even in the hot liquid on the introduction of a crystal of  $\beta$ -methylmorphimethine. We are greatly indebted to Dr. R. S. Cahn for a specimen of pure  $\beta$ -methylmorphimethine. The neopinemethine crystallised from alcohol in large, twinned, rhombohedral prisms, m. p.  $135^{\circ}$ , and at the same temperature when mixed with  $\beta$ -methylmorphimethine. It dissolved in sulphuric acid to a deep crimson solution, which became royal blue on heating and on dilution with water, green and then yellow with an intense green fluorescence. This reaction is characteristic of  $\beta$ -methylmorphimethine.

*Neopinemethine methiodide* was prepared from the methine before the latter had been crystallised. The substance crystallised from

water in glistening needles, m. p.  $291^{\circ}$  (decomp.) after darkening from  $260^{\circ}$  (Found : I, 27.8. Calc., I, 27.9%). Knorr and Smiles (*Ber.*, 1902, 35, 3010) and Knorr and Hawthorne (*Ber.*, 1902, 35, 3012) found that  $\beta$ -methylmorphimethine methiodide had  $[\alpha]_D^{25} + 233^{\circ}$  ( $c = 0.6$ ) in 97% and 90% alcohol. Solutions of neopinemethine methiodide having a similar concentration crystallised on cooling, but we now know that neopinemethine is  $\beta$ -methylmorphimethine in an exceptionally pure condition. We found that neopinemethine methiodide had  $[\alpha]_D^{25} + 241.1^{\circ}$  ( $c = 0.506$ ) in absolute methyl alcohol and  $[\alpha]_D^{25} + 262.0^{\circ}$  ( $c = 0.3$ ) in 90% ethyl alcohol.

We desire to thank the Ramsay Memorial Trust for a Fellowship (Netherlands) which enabled one of us to take part in this investigation, and for a similar reason we are also grateful to the Royal Commissioners of the Exhibition of 1851 for a Scholarship.

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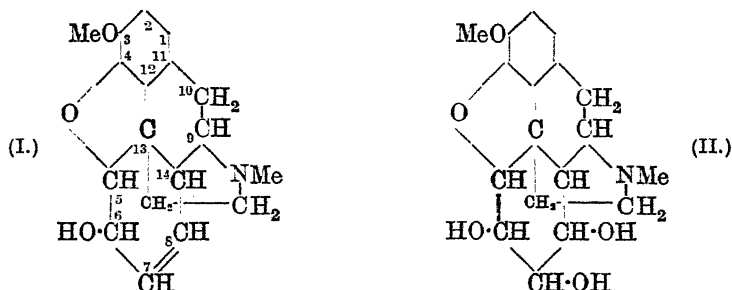
[Received, February 3rd, 1926.]

## CXXVI.—*The Morphine Group. Part IV. A New Oxidation Product of Codeine.*

By ROBERT SIDNEY CAHN and ROBERT ROBINSON.

THE secondary alcohol codeine can be oxidised to the corresponding ketone by means of chromic acid or of potassium permanganate in acetone solution, and apart from the hydroxycodine which accompanies codeinone in the former case (Ach and Knorr, *Ber.*, 1903, 36, 3067) no other products of direct oxidation of the base have been described. This has perhaps led to the impression that the attack of oxidising agents is invariably on the alcoholic group, although attention has occasionally been directed to the fact that the sensitiveness of codeine to permanganate is greater than that of any known saturated alcohol and strongly suggests the existence of an ethenoid group in the molecule (compare Wieland and Kotake, *Annalen*, 1925, 444, 69; Gulland and Robinson, *Mem. Manchester Phil. Soc.*, 1925, 69, No. 10). The remarkable ease with which codeine may be converted into a dihydro-derivative by catalytic hydrogenation is in harmony with this hypothesis, and we now bring forward further evidence tending in the same direction. The action of potassium permanganate on codeine (I) in very dilute aqueous solution leads to the addition of two hydroxyl groups to the molecule and the product is dihydroxydihydrocodeine (II). This substance yields a basic triacetyl derivative and its form-

ation demonstrates the existence of an ethylenic linking in codeine. The position chosen for the double bond in (I) is that independently



selected by Wieland and Kotake and by Gulland and Robinson for different reasons. It is especially required to explain the codeine- $\psi$ -codeine change (analogy to geraniol-linalool) and the reactivity of the chlorine atom of chlorocodide (analogy to allyl chloride and benzyl chloride). A possible objection (compare Gulland and Robinson, *loc. cit.*) is that  $\psi$ -codeinone reacts with benzaldehyde as if it contained the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$ , whereas it should contain  $\cdot\text{O}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot$  on the suggested basis. The difficulty is removed by recognising the following system of tautomerides :

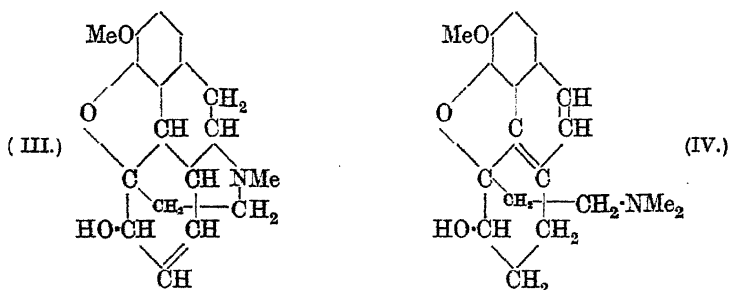


which might be equilibrated in presence of alcoholic potassium ethoxide or similar reagents. Although it seems probable that general agreement will soon be reached in regard to the occurrence of the group  $\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot$  in codeine and its isomerides, and the morphine problem will be to that extent simplified, there is still room for differences of opinion in regard to the point of attachment of the ethanamine chain. Wieland and Kotake (*loc. cit.*) have noted that some substances which on the basis of (I) should contain the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot$  nevertheless have only one reactive position \* and prefer the formula (III) for codeine.

On the other hand, a consideration of the behaviour of the unsaturated centres in the methylmorphimethines appears to us to provide further evidence favouring the formula (I). If (III) represented codeine, we imagine that  $\beta$ -methylmorphimethine would be

\* The attachment of the ethanamine chain in position 13, as in (I), was not based on the production of dipiperonylidene derivatives of thebainol and dihydrothebainone but on the arguments put forward in Part I of this series, to which, with the modification made in our note in the *Manchester Memoirs*, we adhere.—J. M. G., R. R.

(IV), a naphthalene derivative. That the bond migrating from the position 7—8 should halt in the position 8—14 and not proceed to



13—14, where it assists in the formation of a new aromatic nucleus, seems highly improbable. Now  $\beta$ -methylmorphimethine appears to contain non-aromatic unsaturated centres, since it very readily reduces permanganate, more readily than neopine\* does, and on catalytic hydrogenation gives a 9:10-dihydro-derivative (von Braun, *Festschr. phys. Ver.*, Frankfurt a. M., 1924, Sept.; Cahn, *Dissert.*, Frankfurt, 1925). The formula (I), on the other hand, affords a satisfactory explanation of the relations of codeine, neopine, and  $\alpha$ - and  $\beta$ -methylmorphimethines.

#### EXPERIMENTAL.

*Dihydroxydihydrocodeine* (II).—An aqueous solution of potassium permanganate (332 c.c. of 1%) was added during 1.5—2 hours to a mechanically stirred solution of codeine† (10 g.) in water (1500 c.c.) mixed with ice (500 g.) and cooled in an ice-bath. The manganese dioxide was precipitated from the colloidal solution by passing carbon dioxide for  $\frac{1}{2}$  hour and stirring for a further equal period, and the almost colourless filtered liquid was then concentrated to about 400 c.c. by distillation under diminished pressure. Much frothing and decomposition occurred. By means of ether codeine (1.4—1.6 g.) was extracted from the dark brown solution, which was then concentrated to about 40 c.c. and treated with saturated aqueous potassium carbonate (150 c.c.), a semi-solid, almost black material being precipitated. The mixture was twice extracted with 200 c.c. of chloroform, and the solutions were dried with sodium sulphate and evaporated, leaving 5 g. of an amorphous, hygro-

\*  $\beta$ -Methylmorphimethine is also neopinemethine (Van Duin, Robinson, and Smith, this vol., p. 903).

† A similar experiment was carried out with  $\psi$ -codeine, but necessarily in much more dilute solution owing to the sparing solubility of the base in cold water. A large fraction of the  $\psi$ -codeine was recovered and no other crystalline product was isolated.



scopic, dark brown residue (A), which was taken up in dry ethyl alcohol (15 c.c.). Crystallisation was induced by rubbing and after some hours the crude base (1.2 g. or 11.5%) was collected and twice recrystallised from absolute alcohol (yield 0.6 g.) in colourless, glistening, diamond-shaped plates, m. p. 208—209° (Found in material dried in a vacuum at 100°: C, 64.8; H, 7.0; N, 4.5; MeO, 9.4.  $C_{18}H_{23}O_5N$  requires C, 64.8; H, 7.0; N, 4.2; MeO, 9.3%). This substance is easily soluble in water to strongly alkaline solutions but, when pure, it is not very hygroscopic; it is sparingly soluble in ether and benzene and in cold anhydrous methyl or ethyl alcohol. The base does not exhibit many of the colour reactions characteristic of codeine; with Froehde's reagent, it yields a yellow solution which becomes brown on warming, and with Mandelin's reagent it gives a brown solution which on gently warming becomes light green. Unlike codeine, it is only slowly attacked by potassium permanganate in dilute aqueous solution. The salts of this base, including the methiodide, were not obtained in a crystalline condition. As the substance has the same state of oxidation as codeinone and thebaine, a specimen was submitted to the action of hydrochloric acid under the conditions which are employed for the preparation of thebenine from thebaine, but no change occurred. The low yield of the trihydroxy-base is probably due to side reactions, further oxidation and possibly the production of stereoisomerides.

The *triacetyl* derivative is characteristic and may be most conveniently obtained from the material (A) mentioned above. 3 G. of this, heated with acetic anhydride (30 c.c.) for 75 minutes on the steam-bath, gave a brown solution which was decomposed with water, rendered alkaline by ammonia and extracted with chloroform. After removal of the solvent the residue was dissolved in methyl alcohol (10 c.c.) and the crystals which separated on cooling were collected (0.3 g.) and recrystallised from methyl alcohol in colourless plates, m. p. 200° (Found in material dried at 100° over phosphoric anhydride in a vacuum: C, 62.9; H, 6.6; N, 3.3.  $C_{24}H_{29}O_8N$  requires C, 62.7; H, 6.4; N, 3.1% and  $C_{22}H_{27}O_7N$  requires C, 63.3; H, 6.5; N, 3.4%). As the analytical results were in approximate agreement with the theoretical requirements of the formulæ of both the diacetyl and the triacetyl derivative of the parent base, it was vitally important to estimate the acetyl groups directly. We are greatly indebted to Professor K. Freudenberg and Dr. E. Weber, who have kindly carried out the estimations by a new micro-analytical method (Freudenberg, *Annalen*, 1923, 433, 230; Freudenberg and Weber, *Z. angew. Chem.*, 1925, 38, 280) [Found:  $CH_3CO$ , 27.93, 27.78, 27.87.  $C_{18}H_{20}O_5N(COCH_3)_3$

requires  $\text{CH}_3\cdot\text{CO}$ , 28.09%]. The acetyl groups were somewhat resistant to hydrolysis, and two distillations were necessary; the standard process gave  $\text{CH}_3\cdot\text{CO}$ , 24.6%. This might suggest that one of the acetyl groups is attached to nitrogen, were it not for the fact that the substance is a strong base readily soluble even in dilute acetic acid. A compound identical with the above-described derivative was obtained by acetylation of pure dihydroxydihydrocodeine.

Triacetyldihydroxydihydrocodeine is sparingly soluble in water and in cold methyl alcohol; its *perchlorate* crystallises from water in slender, colourless needles, m. p.  $281^\circ$  with slight previous decomposition.

We are indebted to the Department of Scientific and Industrial Research for grants which have enabled one of us to take part in this investigation.

THE UNIVERSITY, MANCHESTER.

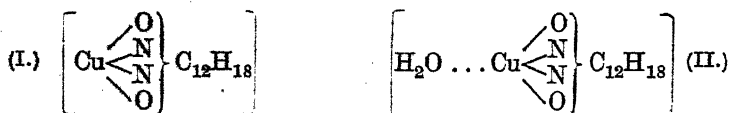
[Received, March 5th, 1926.]

### CXXVII.—*Researches on Residual Affinity and Co-ordination. Part XXVI. A Quadridentate Group in Combination with Bivalent Metals.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN the preceding communication of this series we showed that ethylenediaminobisacetylacetone, first prepared by Combes, furnishes a bivalent quadridentate radical which is capable of behaving as a fourfold associating group in co-ordination compounds of the metals. This fact was demonstrated by a study of the co-ordination compounds of bivalent and trivalent cobalt and the investigation has now been extended to the corresponding derivatives of bivalent copper, nickel, and palladium.

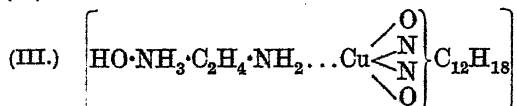
Cupric ethylenediaminobisacetylacetone, prepared originally by Combes (*Compt. rend.*, 1889, 108, 1252), is a well-defined, highly crystalline, dark violet derivative behaving as a non-ionised complex containing one bivalent copper atom in combination with one molecular proportion of the bivalent quadridentate radical. Its constitution may be expressed by formula (I), in which the quadri-



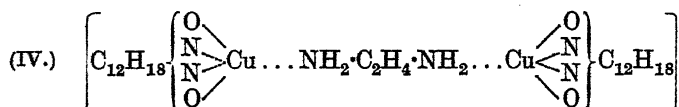
dentate radical is grouped round the metallic atom either tetrahedrally or at four points in one plane. It is, however, not possible

to decide between these possibilities, because in either case the co-ordination complex is unsaturated and readily takes up another associating unit as when the anhydrous violet copper compound absorbs water to pass into its dark green monohydrate (II).

Other addenda can be added in a similar manner to the unsaturated complex, for when Combes's violet compound is dissolved in ethylenediamine hydrate, combination occurs with one molecular proportion of the solvent, giving rise to an analogue (III) of the foregoing aquo-derivative (II).



This ethylenediaminehydrato-compound, when exposed in a desiccator over solid caustic soda or calcium chloride, loses all its water and half of its ethylenediamine, giving rise to the anhydrous ethylenediamine derivative (IV), in which two molecular proportions of Combes's compound are associated with one molecule of ethylenediamine.



It is evident from the existence of these three compounds (II, III, and IV) that one characteristic co-ordination number of copper is 5. This conclusion is borne out by the preparation of a stable light green mono-quinoline derivative of copper acetylacetonate,  $[Cu(C_5H_7O_2)_2, C_9H_7N]$  (V). Similar compounds are obtainable from ammonia and pyridine, but the derivatives of these more volatile bases are unstable, losing their addenda rapidly at the ordinary temperature.

#### *Co-ordination Numbers of Bivalent Copper.*

The literature of copper compounds exhibiting residual affinity is very extensive and furnishes many diverse examples of addenda in these copper derivatives varying in number from 1 to 6, with indications of even higher values. Among the lower values, 2 and 3 stand out prominently and are represented by compounds sufficiently stable and well-defined to warrant the belief that there are copper complexes corresponding with co-ordination numbers 2 and 3. There are also numerous and varied examples among copper compounds of the higher even co-ordination numbers 4 and 6.

The results obtained in this investigation with regard to the formation of complexes with co-ordination number 5 warrant a

reconsideration of the constitutions often accepted for such substances as the following:  $\text{CuCl}_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ ;  $\text{CuBr}_2 \cdot 5\text{NH}_3$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ;  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ ;  $\text{CuSO}_4 \cdot 5\text{NH}_3$  and  $\text{CuSO}_4 \cdot 5\text{NH}_2 \cdot \text{OH}$ .

In formulating these copper salts as co-ordination compounds, at least two alternative views present themselves. The associating units may be grouped exclusively round the metallic atom, giving rise to complex cations of the general type  $[\text{Cu}5\text{X}]^{+}$  or contrariwise one or more molecules of the various addenda may be wholly or partly associated with the anions, which thus become hydrated or ammoniated. If the latter condition could be demonstrated in any of these instances, then the co-ordination number for copper would, in such cases, become less than 5.

There are, however, other less equivocal examples of five associating units round copper in which the metallic atom is no longer in a cation but in an anion such as in pentachlorocupric acid,  $\text{H}_3[\text{CuCl}_5]$  (G. Naumann, *Monatsh.*, 1894, **15**, 489) and in the double nitrites  $\text{K}_2[\text{Cu}(\text{NO}_2)_5]$  and  $\text{Rb}_2[\text{Cu}(\text{NO}_2)_5]$  (Kurtenacker, *Z. anorg. Chem.*, 1913, **82**, 204) and  $\text{Ti}_3[\text{Cu}(\text{NO}_2)_5]$  (Cuttica and Paciello, *Gazzetta*, 1922, **52**, i, 141).

Further evidence on this type of copper co-ordination is now under investigation, particularly in regard to complexes derived from cupric iodide. These results, which indicate a descent from 6 to 5 in the number of associating units round bivalent copper, will shortly be submitted.

### *Electronic Structure of the Bivalent Copper Atom.*

The foregoing evidence, which points to 5 as a characteristic co-ordination number for bivalent copper, has been shown by one of us (J. D. M. S.) to be a consequence of the electronic distribution in atoms first propounded two years ago (Main Smith, *J. Soc. Chem. Ind.*, 1924, **43**, 323). According to this general scheme, which was then applied to all elements, the probable structure of the bivalent cupric ion was shown to be 2, 224, 22445, 000, using ciphers to indicate the vacant sub-groups to be filled by electrons derived from associating units.

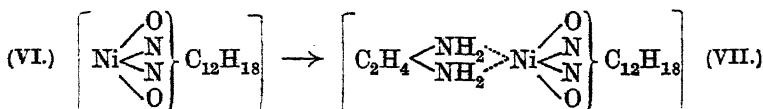
Then if, in combination with a quadridentate group, each associating atom of the group contributes two electrons to the three empty electronic sub-groups of the cupric ion, the electronic structure of the co-ordinated atom will be 2, 224, 22445, 224. This arrangement differs from the electronic structure 2, 224, 22446, 224 for the atom of krypton, the inert gas next higher than copper in atomic number, only in a shortage of one electron in the 9th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated cupric atom with co-ordination

number 4. If this incomplete 9th sub-group could be completed by the addition of a single electron (Main Smith, *J. Soc. Chem. Ind.*, 1925, 44, 944) from the fifth associating unit of a copper co-ordination compound, then the cupric atom of co-ordination number 5 would possess the electronic structure 2, 224, 22446, 224, identical with that of the inert gas krypton.

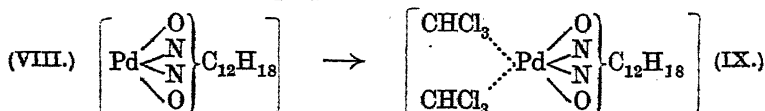
*Co-ordination Numbers of Bivalent Nickel and Palladium.*

The bivalent quadridentate group from ethylenediaminobisacetylacetone also furnishes well-defined, stable derivatives of bivalent nickel and palladium.

*Nickel ethylenediaminobisacetylacetone* (VI), which melts and even boils without decomposition providing that air is excluded, resembles Combes's copper derivative and is an unsaturated substance forming additive compounds with two molecular proportions of ammonia or with one of ethylenediamine. The latter combination is the more stable of the two, its constitution being indicated by formula (VII).



*Palladous ethylenediaminobisacetylacetone* (VIII) is a fairly stable, non-ionised complex insoluble in water but dissolving in the ordinary organic solvents. From these media it separates with addenda of crystallisation. The dichloroformo-derivative, for example (IX), contains two molecular proportions of solvent.



The foregoing results indicate that nickel and palladium have a co-ordination number 4 in their combinations with the bivalent quadridentate group, but these compounds are unsaturated and take up addenda, suggesting that bivalent nickel and palladium have also the higher co-ordination number 6, displayed, however, in less stable derivatives.

*Electronic Structures of the Bivalent Nickel and Palladium Atoms.*

Nickel and bivalent palladium have yielded simple derivatives with ethylenediaminobisacetylacetone, in which the co-ordination number 4 is apparent as in Combes's simple cupric compound, and they further resemble the latter also in being co-ordinatively unsaturated, yielding addition compounds with various addenda, such as ammonia, ethylenediamine, and chloroform.

According to the general scheme of atomic structure above mentioned, the bivalent nickel atom has the probable electronic structure 2, 224, 22444, 000. If the quadridentate group, as with copper, adds four pairs of electrons to the three empty sub-groups, the electronic structure for the co-ordinated nickel atom will be 2, 224, 22444, 224. This differs from the electronic structure for the atom of the inert gas, krypton, only in a shortage of two electrons in the 9th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated nickel atom with co-ordination number 4.

The electronic structure of the bivalent palladium atom in the above scheme is 2, 224, 22446, 22444, 000, resembling that of the nickel atom with the interpolation of five sub-groups 22446. If the quadridentate group as before adds four pairs of electrons to the three empty sub-groups, the electronic structure for the palladous atom becomes 2, 224, 22446, 22444, 224. This differs from the structure of the inert gas, xenon, 2, 224, 22446, 22446, 224, only in a shortage of two electrons in the 14th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated palladous atom with co-ordination number 4.

Both nickel and palladous atoms in combination with the quadridentate group, however, yield addition compounds with two molecules or equivalents of ammonia, chloroform, and anhydrous ethylenediamine, and thus differ from the cupric compounds, which yield addition compounds with only one molecule or equivalent of the addenda. As in the case of copper, the addenda for nickel and bivalent palladium atoms may be regarded as due to the intervention of only one electron per bond, for the addenda are even more feebly attached to the metallic atom than in the case of copper. This conclusion is supported by the very numerous cases of organic and inorganic stable nickel compounds having the co-ordination number 4, which yield much less stable addition compounds having the co-ordination number 6. Typical examples are found in nickel acetylacetonate,  $\text{Ni}\{(\text{OCMe})_2\text{CH}\}_2$ , and nickel tetrammines,  $\text{Ni}(\text{NH}_3)_4\text{X}_2$ , which yield much less stable addition compounds with two molecules or equivalents of water, ammonia or ethylenediamine. If, as suggested, the addenda are held by bonds of only one electron as in the case of copper, the addenda add only two electrons to the 9th sub-group of the nickel structure and two electrons to the 14th sub-group of the palladous structure, thus yielding atomic structures identical in electronic arrangement with those of the inert gases, krypton and xenon, respectively.

These considerations give powerful mutual support to the view that the characteristic co-ordination number is 5 for the cupric

atom, and 6 for the nickel and palladous atoms, and to the above-mentioned scheme of distribution of electrons in atoms and in particular to the electronic structures assigned to the atoms of copper, nickel, and palladium.

*Constitution of Ethylenediamine Hydrate.*

It may be inferred from the knowledge that the co-ordination number of the cupric atom is 5 in addition compounds of cupric complexes with a quadridentate group, that the ethylenediamine hydrate addition compound herein described has the constitution  $\text{ecCuNH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3 \cdot \text{OH}$ , the ethylenediamine hydrate molecule not being a chelate group and being attached to the cupric atom by only one nitrogen atom, and the molecule of water being in consequence necessarily combined with the other nitrogen atom. This view is supported by the fact that on dehydration a compound of chelate ethylenediamine and the cupric atom with the co-ordination number 6 is not obtained. The product contains per cupric atom only half a molecule of ethylenediamine, which is thus still not a chelate group but has the two nitrogen atoms combined with separate cupric atoms having the co-ordination number 5. This product is obtained only by the loss of water and ethylenediamine hydrate simultaneously from two molecules of the original compound, thus indicating that the water molecule of the original compound is not in combination with the cupric atom and is firmly attached to only one nitrogen atom.

Ethylenediamine hydrate is an exceedingly stable substance and is a base nearly as strong as the alkalis, indicating that it has the constitution of an ammonium hydroxide,  $(\text{C}_2\text{H}_4\text{N}_2\text{H}_5)\text{OH}$ . As ethylenediamine does not give rise to basic salts containing only one molecule of acid per molecule of base, it follows that the two basic amino-groups are completely equivalent, and that separation of the water molecule can only be effected by acids on condition that both amino-groups react simultaneously. The two amino-groups consequently must equally share the single hydrogen atom ionised from the hydroxyl group of the hydrate, thus leading to the constitution  $[\text{C}_2\text{H}_4(\text{NH}_2)_2\text{H}]\text{OH}$ . The graphic formula for ethylenediamine hydrate should thus be written :



being a five-membered cyclic structure containing a hydrogen atom with co-ordination number 2.

This formulation is in complete harmony with the known properties of ethylenediamine hydrate and other polymethylenediamine

hydrates, and with the foregoing considerations relating to the ethylenediamine addition compounds of the cupric atom.

### EXPERIMENTAL.

$C_2H_4[N:C(CH_3) \cdot CH:C(CH_3) \cdot O-]_2 = ec$  (dibasic acid radical of ethylenediaminobisacetylacetone).\*

#### 1. Copper Series.

*Aquo-cupric Ethylenediaminobisacetylacetone*,  $H_2O$  Cu $ec$ .—On adding a solution of ethylenediaminobisacetylacetone to an aqueous ammoniacal solution of any cupric salt, glistening, bright violet scales of Combes's anhydrous cupric ethylenediaminobisacetylacetone,  $Cu\ ec$ , are immediately and quantitatively precipitated, but when left in contact with the mother-liquor or on exposure of the damp salt to moist air, the violet scales are wholly transformed into transparent scales varying from sage to dark green in colour. This green salt is the monohydrate of Combes's salt and is the sole product formed when the purple solution of Combes's salt in acetone is poured into dilute aqueous ammonia solution. When the pale blue cupric salt of acetylacetone undergoes prolonged treatment with aqueous ethylenediamine, a simple ethylenediammino-addition compound is not formed, although the copper salt dissolves to an indigo-blue solution. From this solution the green hydrate of Combes's salt alone separates, the ethylenediamine undergoing organic condensation with two molecules of acetylacetone, the aminated dienolic diketone being formed in combination with the cupric atom by elimination of water (Found: N, 9.2; Cu, 21.0; loss at  $100^\circ$ , 6.0.  $C_{12}H_{20}O_3N_2Cu$  requires N, 9.2; Cu, 21.0;  $H_2O$ , 5.9%).

*Aquo-cupric ethylenediaminobisacetylacetone*, forming large, black tablets, dark green by transmitted light, is insoluble in water, dissolves in nearly all organic solvents to form purple solutions of the anhydrous salt, and becomes anhydrous at  $100^\circ$ , but is unaffected by dry or moist air at the ordinary temperature. It melts at the temperature of the anhydrous salt,  $137^\circ$ , to a purple liquid, and, out of contact with air, boils at a high temperature without decomposition. The vapour in contact with air deposits a copper mirror on heated glass surfaces.

*Cupric Ethylenediaminobisacetylacetone Ethylenediamine Hydrate*,  $ecCuNH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2 \cdot OH$ .—A hot solution of Combes's anhydrous cupric ethylenediaminobisacetylacetone in ethylenediamine hydrate, on cooling, deposits large, grass-green plates of a new salt in which

\* For certain details of preliminary work on the metallic derivatives of this quadridentate group we are indebted to Dr. H. D. K. Drew.—G. T. M.



one molecule of the cupric salt is combined with one molecule of the ethylenediamine hydrate (Found: Cu, 17.6, 17.4.  $C_{14}H_{28}O_3N_4Cu$  requires Cu, 17.5%).

Cupric ethylenediaminobisacetylacetone ethylenediamine hydrate crystallises from ethylenediamine hydrate in large, grass-green or ivy-green plates, which are slowly decomposed on exposure to air, emitting white fumes of ethylenediamine hydrate and yielding Combes's violet salt. It dissolves to a purple solution in hot benzene, but is reprecipitated unchanged on addition of a mixture of ethylenediamine hydrate and light petroleum, in which it is insoluble. It loses all its water and half of its ethylenediamine on exposure over solid sodium hydroxide, and is converted into a new salt, sage green in colour.

*Ethylenediammino-dicupric Bisethylenediaminobisacetylacetone*,  $C_2H_4(NH_2Cu ec)_2$ .—On exposure of the foregoing bright green addition compound of Combes's violet salt and ethylenediamine hydrate in a confined space over solid caustic soda or fused calcium chloride, fumes of ethylenediamine hydrate are continuously emitted and a green salt is produced in which two molecules of Combes's salt are combined with one molecule of anhydrous ethylenediamine (Found: N, 13.0; Cu, 19.7.  $C_{26}H_{44}O_4N_6Cu_2$  requires N, 13.3; Cu, 20.2%).

Ethylenediammino-dicupric bisethylenediaminobisacetylacetone forms glistening, sage-green scales which are stable in a confined space but are slowly decomposed on exposure to air with the formation of Combes's violet salt; it is insoluble in water and in 2*N*-caustic soda solution, but is slowly decomposed to form Combes's violet salt, and is thus distinguished from the foregoing hydrated salt, which is not decomposed by 2*N*-caustic soda solution and is only very slowly decomposed by water.

*Quinolino-cupric Acetylacetone* (V).—Pale blue cupric acetylacetone was dissolved in boiling quinoline, forming a dark green solution, from which, on cooling, large, sage-green plates separated. These were removed and dried in air (Found: Cu, 15.9.  $C_{19}H_{21}O_4NCu$  requires Cu, 16.3%). This quinoline addition compound is stable in dry air, but is slowly decomposed by moist air and by water, or by solution in organic solvents, quinoline being lost and the simple cupric salt regenerated.

Cupric acetylacetone forms similar sage-green addition compounds with ammonia and with pyridine on addition of an alcoholic solution of the salt to a concentrated aqueous solution of the base, but these more volatile bases are rapidly lost on removal from the precipitating medium and consequently these addition compounds cannot be dried for analysis.

2. *Nickel Series.*

*Nickel Ethylenediaminobisacetylacetone*, Ni ec.—Hexa-aquo-nickel chloride (2.4 g. = 1 mol.) was dissolved in water (20 c.c.) and mixed with ethylenediaminobisacetylacetone (2.2 g. = 1 mol.) in alcoholic solution (29 c.c.), forming a dark reddish-brown liquid, to which was added 5*N*-sodium hydroxide solution (4 c.c. = 2 mols.). An olive-green precipitate separated, which dissolved to a reddish-black solution on heating on the steam-bath, large, brilliant bronze-red, rhomboidal, transparent scales and plates rapidly separating, which were washed with water, recrystallised from alcohol and air-dried (Found: Ni, 20.8.  $C_{12}H_{18}O_2N_2Ni$  requires Ni, 20.9%).

Nickel ethylenediaminobisacetylacetone, crystallising in bronze-red scales or plates or reddish-black tablets, is insoluble in water, readily soluble in most organic solvents to red solutions, and soluble in mineral acids only with decomposition, forming acetylacetone and nickel and ethylenediamine salts. It melts at 200° to a black liquid, and, out of contact with air, boils without decomposition at a temperature approaching a red heat, forming a heavy yellow vapour, which condenses in bright red needles. The vapour, in contact with air, deposits a glistening nickel mirror on a heated glass surface, similar to the cobalt mirror obtained by heating the corresponding cobaltous salt.

*Ethylenediammino-nickel Ethylenediaminobisacetylacetone*,  $C_2H_4(NH_2)_2Ni$  ec.—The foregoing nickel salt was dissolved in the minimum quantity of boiling ethylenediamine hydrate, forming a brownish-red solution, from which, on rapid cooling, elongated, brownish-red needles separated. These were removed, washed with light petroleum and dried over solid caustic soda (Found: Ni, 17.2  $C_{14}H_{26}O_2N_4Ni$  requires Ni, 17.2%).

The acicular form of ethylenediammino-nickel ethylenediaminobisacetylacetone slowly loses ethylenediamine on exposure; it is insoluble in water and decomposed by this medium, forming the foregoing simple salt and a strongly alkaline solution of ethylenediamine.

*Diammino-nickel Ethylenediaminobisacetylacetone*,  $(NH_3)_2Ni$  ec.—On pouring a saturated solution of the simple nickel salt in alcohol into 18*N*-ammonia solution, brilliant red prisms separated. On drying, these rapidly lost ammonia, even over sodium hydroxide and ammonium carbonate. Analysis was possible only of the partly deaminated salt, the highest percentage of ammonia found being 7.9. The diammine requires 10.8 and the monammine 5.7%, indicating that the product was almost certainly the diammino-nickel salt.

3. *Palladous Series.*

*Palladous Ethylenediaminobisacetylacetone.* Pd ec.—Palladous chloride (0.9 g. = 1 mol.) was dissolved in boiling 10*N*-hydrochloric acid, and the solution rather more than neutralised with sodium carbonate. Ethylenediaminobisacetylacetone (1.2 g. = 1 mol.) and 5*N*-sodium hydroxide solution (2 c.c. = 2 mols.) were then added. On heating on the steam-bath, the yellow mixture assumed a brownish-black colour. After cooling, the liquid was filtered, and the solid residue extracted with acetone until the extracts were colourless. On concentrating the orange-coloured acetone extracts, yellow prisms separated, which were recrystallised from benzene and air-dried (Found: N, 8.3; Pd, 32.4.  $C_{12}H_{18}O_2N_2Pd$  requires N, 8.5; Pd, 32.5%).

Palladous ethylenediaminobisacetylacetone forms canary-yellow needles, m. p. 228°. It is insoluble in water, sparingly soluble in light petroleum, and freely soluble in most other organic solvents, from which it separates in pale yellow prisms with solvent of crystallisation, readily lost on exposure, yielding the simple salt.

*Dichloroformo-palladous Ethylenediaminobisacetylacetone,*  $(CHCl_3)_2Pd$  ec.—From a saturated solution of palladous ethylenediaminobisacetylacetone in chloroform, large, elongated, hexagonal, pale yellow tablets separated, which were removed and dried by a very short exposure to air (Found: loss at 100°, 41.7.  $C_{14}H_{20}O_2N_2Cl_6Pd$  requires  $CHCl_3$ , 42.1%). The addition compound, on exposure to air, only slowly loses chloroform (identified by odour), but is rapidly converted into the simple salt by heating for about an hour at 100°.

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### CXXVIII.—*Derivatives of 2-Keto-1:2-dihydrobenzisothiazole.\**

By ERNEST WILSON McCLELLAND and ALBAN JAMES GAIT.

It has been suggested (McClelland and Longwell, J., 1923, 123, 3310) that the first stage in the production of the disulphide (I) from 2-dithiobenzoyl and a primary amine is the formation of

\* Named "2-thiobenzimide" in previous papers.

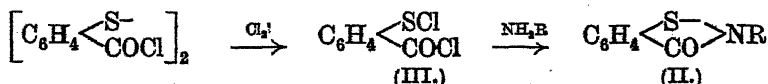
hydrogen sulphide and a ketodihydrobenzisothiazole (II). It was pointed out that these benzisothiazoles, if formed, would be



very easily reduced to the corresponding disulphides and that the failure to isolate them was probably due to their reduction by the hydrogen sulphide.

Such compounds appear to be unknown and the present investigation was undertaken with the object of synthesising them and examining their stability towards hydrogen sulphide.

Attempts to prepare 2-keto-1-phenyl-1:2-dihydrobenzisothiazole by the intramolecular condensation of (I; R = Ph), which in the presence of sulphuric acid might be expected to react as the sulphenic acid,  $NHPh \cdot CO \cdot C_6H_4 \cdot S \cdot OH$  (compare Prescott and Smiles, J., 1911, 99, 640), were unsuccessful. According to patent literature (D.R.P.-ann. F. 35230), 2:2'-dithiobenzoic acid on treatment with chlorine yields a sulphur chloride,  $CO_2H \cdot C_6H_4 \cdot SCl$ . It was therefore to be expected that 2:2'-dithiobenzoyl chloride would also yield a sulphur chloride (III) and that this dichloride would condense with primary amines to give the required *N*-substituted ketodihydrobenzisothiazoles (II) thus:



2:2'-Dithiobenzoyl chloride, suspended in carbon tetrachloride, dissolved on treatment with dry chlorine, presumably owing to the formation of the dichloride (III). This chlorinated solution reacted with aqueous ammonia to give 2-keto-1:2-dihydrobenzisothiazole. In a similar way the chlorinated solution reacted with aniline, *o*-toluidine, and aqueous methylamine to give compounds of the type (II) in which R is Ph, *o*-C<sub>6</sub>H<sub>4</sub>Me, and Me, respectively. On oxidation with hydrogen peroxide these compounds were converted into the corresponding "saccharins." The interaction of the chlorinated solution of 2:2'-dithiobenzoyl chloride with *n*-propylamine yielded an oily substance which was undoubtedly 2-keto-1-*n*-propyl-1:2-dihydrobenzisothiazole, as on oxidation it was converted into *N*-*n*-propyl-*o*-benzoic sulphinide.

The 1-phenyl, 1-*o*-tolyl, and 1-methyl derivatives of 2-keto-1:2-dihydrobenzisothiazole in alcoholic solution are rapidly reduced by hydrogen sulphide with deposition of sulphur and formation of disulphides identical with the products obtained by the action of the corresponding amines on 2-dithiobenzoyl. The afore-mentioned suggestion of McClelland and Longwell hereby receives strong

confirmation. 2-Keto-1:2-dihydrobenzisothiazole also is reduced by hydrogen sulphide. The fact that it can be isolated by the action of ammonia on 2-dithiobenzoyl may be due to its being slightly more stable than its derivatives towards hydrogen sulphide, as previously suggested.

Selenium analogues of 2-keto-1:2-dihydrobenzisothiazole and certain of its derivatives have been prepared by an analogous method (Lesser and Weiss, *Ber.*, 1924, 57, 1077).

#### EXPERIMENTAL.

2:2'-Dithiobenzoyl chloride was prepared by the action of phosphorus pentachloride on 2:2'-dithiobenzoic acid (*Ber.*, 1898, 31, 1670) and was crystallised from benzene before use in the following experiments.

The derivatives of 2-keto-1:2-dihydrobenzisothiazole described below were prepared by the following general method. Dry chlorine was bubbled through a suspension of 2:2'-dithiobenzoyl chloride (5 g.) in carbon tetrachloride (40 c.c.; dried over calcium chloride) until solution was complete. The excess of chlorine having been removed by a current of dry air, the solution was added slowly, with vigorous stirring, to aqueous ammonia (40 c.c.;  $d$  0.880), 30% aqueous methylamine (excess), or the amine (aniline, 8 g.; *o*-toluidine, 10 g.) diluted with carbon tetrachloride. During the addition the aqueous ammonia and the solutions of the amines were cooled in ice. The product of the reaction was either precipitated or obtained by evaporation of the dried carbon tetrachloride solution.

2-Keto-1:2-dihydrobenzisothiazole (II;  $R = H$ ) was precipitated on addition of the chlorinated solution of 2:2'-dithiobenzoyl chloride to the aqueous ammonia and was crystallised from methyl alcohol and finally from water (yield 80%). It melted at 155–156°, alone or mixed with a specimen prepared by the action of ammonia on 2-dithiobenzoyl.

2-Keto-1-phenyl-1:2-dihydrobenzisothiazole (II;  $R = Ph$ ).—In this preparation aniline hydrochloride was precipitated; it was filtered off and the carbon tetrachloride allowed to evaporate at room temperature. The residual solid crystallised from methyl alcohol in fine, colourless needles, m. p. 140° (Found: C, 68.4; H, 4.1; S, 13.9.  $C_{13}H_9ONS$  requires C, 68.7; H, 4.0; S, 14.1%).

2-Keto-1-*o*-tolyl-1:2-dihydrobenzisothiazole (II;  $R = o\text{-C}_6\text{H}_4\text{Me}$ ) was obtained as a brown oil which slowly solidified; after crystallisation from methyl alcohol it melted at 122–123° (Found: C, 69.7; H, 4.5; S, 13.4.  $C_{14}H_{11}ONS$  requires C, 69.7; H, 4.5; S, 13.3%).

2-Keto-1-methyl-1:2-dihydrobenzisothiazole (II;  $R = CH_3$ ) was  

$$H \ H^* \ 2$$

obtained from the carbon tetrachloride after separation from the aqueous solution, as a brown oil which slowly solidified; it crystallised from benzene-light petroleum in fine, colourless needles, m. p. 51—52° (Found: C, 58.0; H, 4.3; S, 19.5.  $C_8H_7ONS$  requires C, 58.1; H, 4.3; S, 19.4%).

This isothiazole is sparingly soluble in ether and light petroleum and very soluble in alcohol or benzene. On treatment with hydrochloric acid the crude oil obtained above yielded a *hydrochloride*, which was readily hydrolysed by water but crystallised from hydrochloric acid in colourless needles, m. p. 124—127°. The hydrochloride appears to be unstable, as varying results were obtained in the estimation of the chlorine and its melting point gradually fell on keeping in a vacuum desiccator.

*N-n-Propyl-o-benzoicsulphinide*,  $C_6H_4 \begin{smallmatrix} SO_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} N \cdot C_3H_7$ .—A chlorinated solution of 2:2'-dithiobenzoyl chloride, prepared by the general method, was added to an excess of propylamine diluted with carbon tetrachloride. The solid material was filtered off, and the carbon tetrachloride evaporated. The oil thus obtained was oxidised in glacial acetic acid with hydrogen peroxide (30%). The product crystallised from water in fine, colourless needles, m. p. 73—75° (Found: S, 14.1; N, 6.1.  $C_{10}H_{11}O_2NS$  requires S, 14.2; N, 6.2%).

*Oxidation of the Benzisothiazoles*.—A solution of 2-keto-1-phenyl-1:2-dihydrobenzisothiazole (0.2 g.) in glacial acetic acid was heated with 30% hydrogen peroxide (1 c.c.) for 1 hour at 100°. On cooling, a white, crystalline product was obtained. This, after recrystallisation from glacial acetic acid, melted at 189—190°, and at 189° when mixed with authentic *N*-phenyl-*o*-benzoicsulphinide, m. p. 190.5° (*Amer. Chem. J.*, 1895, 17, 320).

In a similar way 2-keto-1-*o*-tolyl-1:2-dihydrobenzisothiazole yielded a substance, m. p. 171—173° (*N*-*o*-tolyl-*o*-benzoicsulphinide has m. p. 172—175°; *loc. cit.*, p. 327).

2-Keto-1-methyl-1:2-dihydrobenzisothiazole (the crude oil) was instantly converted by cold hydrogen peroxide (30%) into a white, crystalline substance. This, after recrystallisation from glacial acetic acid and finally from methyl alcohol, melted at 129—130°, alone or mixed with *N*-methyl-*o*-benzoicsulphinide.

*Reduction of the Benzisothiazoles*.—Hydrogen sulphide was bubbled slowly through a solution of 2-keto-1-phenyl-1:2-dihydrobenzisothiazole in ethyl alcohol at 50°. In a few minutes a precipitate of sulphur appeared; the current of gas was then stopped, and the solution filtered as quickly as possible. The filtrate slowly deposited colourless needles contaminated with sulphur. After several crystallisations from glacial acetic acid, the product was obtained free from

sulphur; it melted at 236—238°, and at 237° when mixed with 2 : 2'-dithiobenzophenylamide (m. p. 239°), prepared by the action of aniline on 2-dithiobenzoyl.

2-Keto-1-*o*-tolyl-1 : 2-dihydrobenzisothiazole, reduced in a similar way, gave a product which after recrystallisation from methyl alcohol melted at 219—220°, alone or mixed with the product obtained by the action of *o*-toluidine on 2-dithiobenzoyl.

The reduction of 2-keto-1-methyl-1 : 2-dihydrobenzisothiazole by hydrogen sulphide, under the same conditions, yielded a substance which after crystallisation from glacial acetic acid and methyl alcohol melted at 220—221°, alone or mixed with 2 : 2'-dithiobenzomethylamide, prepared by the action of methylamine on 2-dithiobenzoyl.

The authors desire to express their thanks to Professor Smiles for the interest he has taken in this work and for his helpful suggestions.

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## CXXIX.—*The Vapour Pressures of Chlorine Dioxide.*

By FREDERICK ERNEST KING and JAMES RIDDICK PARTINGTON.

A CONNECTED series of measurements of the vapour pressures of chlorine dioxide from the melting point to the boiling point of the substance does not appear to have been recorded. A few isolated measurements, in poor agreement, are given in the literature. Millon (*Ann. Chim. Phys.*, 1843, 7, 314; *Annalen*, 1843, 46, 281) gives + 20° or + 32° as the boiling point, but does not describe the method used. He correctly states that chlorine dioxide attacks mercury, and dissolves in concentrated sulphuric acid to a bright yellow solution, but his assertion that the latter decomposes at 10° with evolution of chlorine, oxygen, chlorine dioxide, and "chlorine trioxide" we do not confirm. Millon also correctly described the colour of liquid chlorine dioxide as red, "like the brightly-coloured sulphur chloride," i.e., the monochloride containing excess of chlorine, but he overestimated the explosive properties of the liquid. Brandau (*Annalen*, 1869, 151, 340) gives the boiling point of what he calls chlorine trioxide as 8—9° at 745 mm.: the substance must have been the dioxide. Pebal (*ibid.*, 1875, 177, 1) determined the boiling point by a rather crude method as 8.7° at 725.7 mm. Schacherl (*ibid.*, 1881, 206, 68) attempted to determine the vapour pressure by means of a mercury manometer in direct communication with a water manometer, the metal being protected from the gas

by a long column of water. Schacherl first noticed that liquid chlorine dioxide, although exploding violently when the process is initiated, is not liable to spontaneous, erratic detonation, as asserted by Millon, provided that all traces of organic matter are excluded and the substance is manipulated entirely in glass. Schacherl gives the following pressures, which are really those over a saturated solution, although he remarks that the yellow colour of the solution had not passed round the water limb of the manometer before the conclusion of the measurements.

$t^{\circ}$ .....	10.6	7.6	9.6	14.0	14.1	16.9	10.3	7.6
$p$ (mm.) .....	767.8	723.8	734.4	961.9	983.9	1162.7	1335.6	1329.1

It is quite clear, as Schacherl himself admits, that these values are completely vitiated by decomposition of the gas at the higher temperatures, and that the first value only can be taken into account. He concluded that the vapour-pressure method must be abandoned as unsuitable for the determination of the boiling point. This was really an incorrect conclusion, since, if he had taken care not to raise the temperature too far above the boiling point, there would probably have been very little decomposition. Schacherl then made a direct estimation of the boiling point with a mercury thermometer bulb immersed in the liquid contained in a small open bulb in a water-bath. The temperature rose slowly to  $9.9^{\circ}$ , remained constant for a short time, then varied between  $9.9^{\circ}$  and  $10.1^{\circ}$ , then returned to  $9.9^{\circ}$ , and remained constant until practically all the liquid had evaporated. The pressure was 730.9 mm. The liquid, it was found, could be boiled rapidly at  $+30^{\circ}$  without explosion, and the vapour recondensed by cooling at  $8.9^{\circ}$ . During the boiling-point determination, care was taken to avoid superheating, and the liquid during the whole series of measurements boiled steadily without bumping.

#### EXPERIMENTAL.

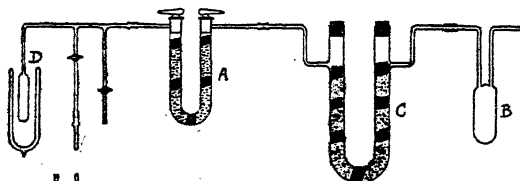
The chlorine dioxide was prepared by a method stated by Spring (*Bull. Acad. roy. Belg.*, 1875, 39, 882) to yield chlorine trioxide, a substance up to the present unknown. The method involved the action of chlorine on dry silver chlorate. We have convinced ourselves that the only gaseous products of this reaction are chlorine dioxide and oxygen, so that it probably proceeds according to the equation  $2\text{AgClO}_3 + \text{Cl}_2 = 2\text{AgCl} + 2\text{ClO}_2 + \text{O}_2$ . The chlorine dioxide is easily liquefied out of the gas by cooling and can be obtained pure and dry.\*

\* Garzarolli Thurnlackh (*Annalen*, 1881, 209, 184) refers to Spring's work at the end of his paper and suggests that the gas may have been a mixture of the composition  $\text{Cl}_2\text{O} + 4\text{ClO}_2$  rather than  $\text{Cl}_2\text{O}_3$ . He promised to investigate the matter further, but does not appear to have done so.



According to Spring, the reaction begins in the cold, but we have found that it is quite inappreciable below about  $80^{\circ}$  and occurs regularly and smoothly at about  $90^{\circ}$ . The silver chlorate was prepared from chloric acid and silver oxide, dried in a desiccator over phosphorus pentoxide, and then about 10 g. were filled into a U-tube with ground stopcocks (A, Fig. 1), with alternate plugs of dry glass wool. Ramsay lubricant proved to be efficient for the ground joints and stopcocks; it was only very slightly attacked, if at all, during the few hours necessary for actual measurements. Pure dry chlorine, liberated by warming liquid chlorine (from potassium permanganate and hydrochloric acid) in a bulb, B, and dried by passing over phosphorus pentoxide in the tube C, was passed slowly over the chlorate, the tube A being maintained at  $85-95^{\circ}$  in an electrically heated air-bath. With fresh chlorate, the reaction was slow at

FIG. 1.



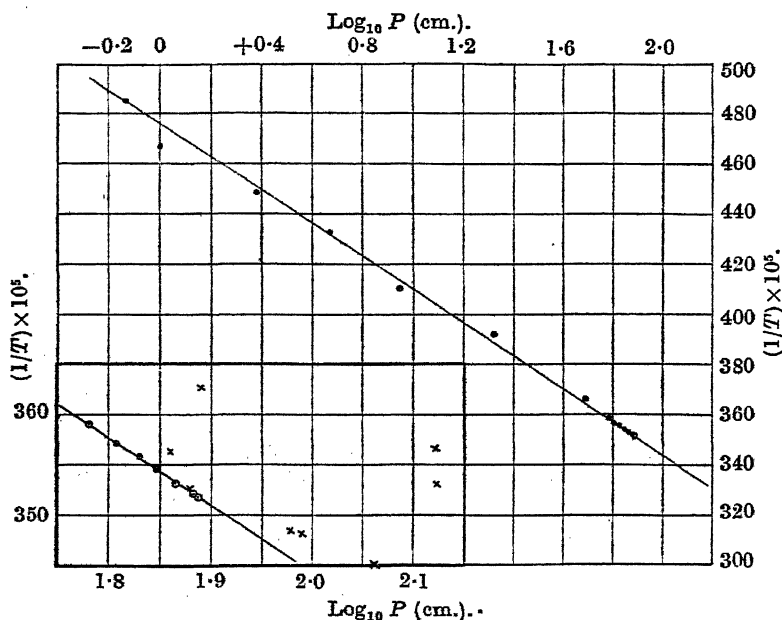
first and some free chlorine tended to pass over. The issuing gas was then passed to a small bulb, D, immersed in solid carbon dioxide and ether, communicating with a pump and two manometers. These contained mercury covered with concentrated sulphuric acid. The first (not shown) served to indicate the pressure after exhaustion and during filling; the second, which was closed by a tap until the actual measurements were begun, served to measure the pressures. By working in this way, excessive attack of the mercury surface used for measurement was avoided. The columns of acid were of the same length in each limb so as to compensate each other. We satisfied ourselves that, although mercury is attacked with the deposition of a white powder, no permanent gas is evolved from the sulphuric acid, which slowly becomes bright yellow in colour. The oxygen accumulating was removed from time to time by pumping.

The chlorine dioxide condensed in the bulb as a crystalline solid of the colour of potassium dichromate. If any excess of chlorine had passed through, this either floated unchanged on the surface of the solid dioxide or condensed along with dioxide to a deep red liquid which did not solidify in the freezing mixture. In either case, the chlorine was easily removed by pumping for a few minutes with

the bulb immersed in the freezing mixture. The pressure finally fell suddenly and the red crystals remained. The vapour pressure of the solid at  $-80^{\circ}$  was negligible.

By adding ether to the freezing mixture until all the solid carbon dioxide had disappeared, it was possible to raise the temperature slowly in steps to  $-30^{\circ}$ . Melting occurred sharply at  $-59^{\circ}$ , both solid and liquid being at first present, and all the solid melted at this temperature. This result is in agreement with the only previous observation, that of Faraday (*Phil. Trans.*, 1845, 135, 155), who found the melting point  $-59^{\circ}$ .\*

FIG. 2.



By further addition of ether, the temperature was gradually raised, the temperatures being measured on a pentane thermometer. After  $-30^{\circ}$ , a mixture of ice and salt, pure ice, and water were used successively, with a mercury thermometer.

The gauge pressures were subtracted from the mercury column reading corresponding with the vacuum attained in the apparatus before admitting gas. After the measurements, the chlorine dioxide was resolidified by immersing the bulb in solid carbon dioxide and

\* Faraday's result is given in most works of reference as  $-76^{\circ}$ ; this, however, is the temperature on the Fahrenheit scale used by Faraday. The correct figure is given in Watts' Dictionary, 1890, vol. 2, p. 13.

ether, and the original vacuum recovered, showing that decomposition had not occurred during the measurements.

The logarithms of the pressures recorded in Table I are plotted against the reciprocals of the absolute temperatures in Fig. 2, and it will be seen that a fair approach to a straight line is obtained. The part near the boiling point is drawn on an enlarged scale to the left. It so happened that the barometric pressure corresponded exactly with 760 mm. when the boiling point was reached, so that the value of the latter,  $11.0^\circ$ , could be determined directly.

The isolated points observed by Pebal and Schacherl are also shown. The first measurement of the latter in the vapour pressure series, when corrected for the vapour pressure of water at  $15^\circ$ , lies almost on the curve, but the remaining measurements show great irregularity. The direct measurement of the boiling point made by Schacherl, *viz.*,  $9.9^\circ/730.9$  mm., also lies on the curve.

TABLE I.

$T^\circ$ Abs. ....	193	206	214*	223	232.5	243.5	255	273
$p$ mm. obs. ...	‡	7	10	24	47	88	201	490
$T^\circ$ Abs. ....	278.3	279.9	281	282	283	284†	284.2	
$p$ mm. obs. ...	608	642	674	700	732	760	769	

\* Melting point.

† Boiling point.

‡ Not measurable.

From the values of the vapour pressures at different temperatures, it is possible to calculate the latent heat of evaporation of liquid chlorine dioxide by means of the formula :

$$\lambda = 4.576 \{ \log(p_2/p_1) \} T_1 T_2 / (T_2 - T_1) \text{ cal. per mol.}$$

From data near the boiling point the value 6520 is obtained. From this, by division by the absolute boiling point  $T_0$ , we find the Trouton coefficient  $\lambda/T_0$  of 23. The values of this calculated by the two formulæ of Nernst are :

$$8.5 \log T_0 = 20.85 \text{ and } 9.5 \log T_0 - 0.007 T_0 = 21.3,$$

and from Wartenberg's formula  $7.4 \log T_0 + 1.985 = 20.2$ .

The ratio of the absolute temperatures corresponding with vapour pressures of 760 mm. and 200 mm. (really 201 mm.) is 1.114, which is the value shown by Ramsay and Young to correspond with normal liquids (*Z. physikal. Chem.*, 1887, 1, 249). These considerations seem to point to very little, if any, association of chlorine dioxide in the liquid state, so that its formula in both the gaseous and the liquid state may be considered to be  $\text{ClO}_2$ . The colours of the solid, liquid, and gaseous forms would also point to the same conclusion.

CXXX.—*The Oxidation Potential of the System Selenium Dioxide-Selenium.*

By SYDNEY RAYMOND CARTER, JOHN A. V. BUTLER, and  
FRANK JAMES.

SELENIUM dioxide is readily reduced to selenium and it appeared that a study of the oxidation potential of the system selenium dioxide-selenium would furnish interesting data for comparison with that of the analogue: sulphur dioxide-sulphur (Carter and James, J., 1924, **125**, 2231).

Preliminary *E.M.F.* measurements were carried out with various half-elements in combination with the calomel electrode. Each cell contained several platinum foil electrodes, some of which were plain and others platinised. The solid selenium used in cells 2, 3 and 5 was the red amorphous variety. In some cases, the platinum foil was buried in the selenium, whilst in others the selenium was deposited electrolytically.

Cell 1.	(Pt) 0.1 <i>M</i> -SeO <sub>2</sub> ,	0.1 <i>M</i> -Na <sub>2</sub> SeO <sub>4</sub> ,	H <sub>2</sub> O
2.	(Pt) 0.1 <i>M</i> -SeO <sub>2</sub> ,	Se (solid),	H <sub>2</sub> O
3.	(Pt) 0.1 <i>M</i> -SeO <sub>2</sub> ,	Se (solid),	10 <i>N</i> -HCl
4.	(Pt) 0.1 <i>M</i> -SeO <sub>2</sub> ,	Se (in solution),	10 <i>N</i> -HCl
5.	(Pt) Se (solid),	10 <i>N</i> -HCl	

1 and 2 gave ill-defined potentials and they were greatly affected by polarisation. 3 and 4 gave well-defined potentials. In 5, the potential was ill-defined, but on the addition of selenium dioxide it rose several tenths of a volt and became steady.

From these and subsequent experiments it was concluded that a definite potential was exhibited, provided that the solution were strongly acid and that selenium dioxide and selenium were each present in solution. In the case of the selenium, it might be present in quantity to form either a saturated or an unsaturated solution. In this connexion, the solubility of selenium is important and experiment revealed the following facts:

1. Red amorphous selenium was stirred with concentrated hydrochloric acid at 20° for 3 days, but no selenium was dissolved. Moreover, under these conditions no selenium dioxide was formed, although the solution was in contact with air.

2. Selenium is soluble in concentrated hydrochloric acid in presence of selenium dioxide. The solubility of selenium in 0.1*M*-SeO<sub>2</sub> and 11.6*N*-HCl is 1.35 g. per litre (within 5%).

3. The solubility of selenium falls off rapidly with diminishing concentration of acid, and, on dilution of saturated solutions with water, the red amorphous selenium is precipitated.

It was therefore decided to determine the oxidation potential of the system selenium-selenium dioxide-concentrated hydrochloric acid, and to study the influence of changes in concentration of (a) selenium, (b) selenium dioxide.

In order to obtain reproducible values of the *E.M.F.* it was obvious that the quantity of dissolved selenium would have to be carefully controlled.

*Materials.*—Selenium dioxide was prepared by dissolving amorphous selenium (B.D.H.) in concentrated nitric acid and evaporating the solution to dryness. The product was twice sublimed in small quantities in a large crucible and thereby freed from tellurium. Pure amorphous selenium was prepared from the purified selenium dioxide by passing sulphur dioxide through a slightly acid solution; after thorough washing on an asbestos pad, the precipitate was dried in a vacuum. The hydrochloric acid employed throughout was B.D.H., As.T. quality.

*Preparation of Solutions.*—A solution of selenium in concentrated hydrochloric acid containing selenium dioxide was prepared by shaking amorphous selenium with the liquid for several days. The clear solution (deep amber colour) was withdrawn into a pipette through a pad of glass wool and portions were analysed. The stock solution had the following composition: 0.066*N*-SeO<sub>2</sub>, 0.0134*N*-Se, 11.6*N*-HCl. This was used for making up the cell solutions by suitable dilution with hydrochloric acid of the same concentration and addition of the proper amounts of selenium dioxide either as the solid or from the stock solution. The composition of some of the solutions was checked by analysis.

*Analysis.*—The determination of selenium dioxide was based on that of Norris and Fay (Gooch, "Methods in Chemical Analysis," 1912, p. 383) for acid solutions. 10 C.c. of the concentrated acid solution are added to 300 c.c. of ice and water. 50 C.c. of *N*/10-sodium thiosulphate are then run in, the excess being titrated with standard iodine solution, starch paste being used as indicator. This method gave accurate results if the conditions were strictly observed.

The estimation of the amount of dissolved selenium was a more difficult matter. At first, the greater part of the hydrochloric acid was evaporated on the water-bath, and the selenium precipitated by the addition of water. This method gave variable results owing apparently to the volatilisation of a portion of the selenium. The method finally adopted was to dilute 100 c.c. of the solution with a litre of water. The selenium separated in a very finely-divided form which did not settle readily. On adding a few c.c. of a strong solution of potassium chloride, however, the precipitate rapidly

settled in a compact curdy form, which was filtered off through a Gooch crucible, dried at  $110^{\circ}$ , and weighed. Long heating at this temperature caused no loss of weight by volatilisation. The filtrate showed no sign of containing any free selenium. It was colourless and clear, and no perceptible turbidity appeared on further dilution.

Hydrochloric acid was determined in a separate portion by suitable dilution and titration with standard sodium carbonate.

*Electrical Measurements.*—It was feared that the presence of concentrated hydrochloric acid in one half of the cell would give rise to a troublesome liquid boundary and make accurate measurements impossible.

The following type of cell was finally found to be most suitable for the purpose:



This arrangement gave reproducible results and was not liable to fluctuations of more than a few tenths of a millivolt during the experiments. Moreover the boundary potentials are of types which may be evaluated if required.

A stationary junction being used at the  $N\text{-HCl} \mid \text{KCl (sat.)}$  boundary, variations of 0.0025 volt over a 10-minute range were experienced, whilst, with the flowing junction, readings constant to 0.0001 volt during 15 minutes were obtained. This is of interest, since the flowing junction has hitherto been applied to junctions of the type  $\text{HCl} \mid \text{KCl}$  for concentrations of 0.1*N* and *N* (Lamb and Larson, *J. Amer. Chem. Soc.*, 1920, 42, 229). The present work shows how it may be employed advantageously in connecting a saturated potassium chloride solution with highly concentrated acid.

The electrodes were of platinum platinised in the usual way. A fresh electrode took some time to acquire a definite potential, but electrodes that had been immersed in one of the solutions, after being washed once or twice with a fresh solution, rapidly assumed a steady potential. In some preliminary experiments a metre bridge in conjunction with a capillary electrometer was employed. With this arrangement, it was found that the electrodes, particularly in the more dilute solutions, were very readily polarised, even with the small currents which passed in finding the balance point, and took some time to recover the original potential. In the later work a Cambridge ionisation potentiometer was used, giving readings direct to 0.2 millivolt with a sensitive A. M. galvanometer. No

trouble was experienced with this arrangement on account of polarisation.

Three electrodes were placed in the electrode vessel. After use in a few cells an electrode often became irregular and differed from the other two. Fairly frequent replatinising was necessary. The electrode vessel was kept in a thermostat at  $20^{\circ} \pm 0.1^{\circ}$  during the measurements. The saturated calomel electrode was one of a battery of four which were frequently compared and at no time differed by more than 0.25 millivolt. The calomel electrodes were at room temperature. This was determined exactly by a thermometer in the liquid of one of them, at the time of every measurement, and the correction introduced.

*Reproducibility and Constancy.*—Although with the more concentrated solutions the mean potentials were easily reproduced to within a fraction of a millivolt (e.g., cell D), minor fluctuations, usually less than a millivolt, were sometimes observed. On the other hand, the solutions containing the more minute concentrations of selenium exhibited a gradual drift in the potential. This was most apparent in cell C, where a gradual decrease from 0.5452 to 0.5247 volt at  $12^{\circ}$  over a period of 22 hours was observed. This was not due to changes in the immediate vicinity of the electrodes, for only a minute alteration of the potential occurred on shaking the cell. The drift appeared to be due to some decomposition in the cell, which was accelerated by the higher temperature of the thermostat, this being slightly above that of the room. A portion of the solution C, which had remained at room temperature for 24 hours, gave a slightly lower potential than the original reading; when placed in the electrode vessel in the thermostat, its rate of drift was greater. It appeared that the reaction concerned was the reduction of selenium dioxide by hydrochloric acid:  $\text{SeO}_2 + 4\text{HCl} = \text{Se} + 2\text{H}_2\text{O} + 2\text{Cl}_2$ .

The formation of selenium to only a slight extent in this reaction would have an appreciable effect on the selenium concentration at the minute concentrations of the more dilute cells. This supposition was supported by the fact that a stock solution of selenium dioxide in concentrated hydrochloric acid, kept at room temperature, acquired after some days a faint yellow tint. The potential of a platinum electrode in this solution measured against the saturated calomel electrode was 0.614 volt, which would correspond to a selenium concentration of about  $10^{-5}M$ .

*Measurements.*—A typical set of potentiometer readings is in Table I, which gives the observations for three freshly prepared cells, D1, D2 and D3, respectively. (The selenium electrode is positive with respect to the calomel.)

$E(t^\circ)$  is the observed *E.M.F.* when the oxidation cell is at  $20^\circ$  and the calomel electrode is at room temperature,  $t^\circ$ :  $E(20^\circ)$  is the *E.M.F.* after correcting the calomel electrode to  $20^\circ$ .

TABLE I.

$[\text{SeO}_2] = 0.0866$ ,  $[\text{Se}] = 0.00134$ ,  $[\text{HCl}] = 11.6$ .

Cell.	Hrs.	Mins.	$E(t^\circ)$ observed.			$E(t^\circ)$ mean.	$E(20^\circ)$ .
D. 1.		10	0.5738	0.5739	0.5736	} $0.5733$ $t = 13.5^\circ$	0.5720
	1	20	0.5732	0.5732	0.5730		
	3	20	0.5729	(0.5716)	0.5728		
D. 2.		10	0.5723	0.5733	} $0.5734$ $t = 13.0^\circ$		0.5720
		40	0.5742	0.5743			
	1	5	0.5728	0.5728			
	3	5	0.5718	0.5718			
	20	0	0.5678	0.5678			
D. 3.	0	40	0.5734	0.5735	} $0.5729$ $t = 14.5^\circ$		0.5718
	1	35	0.5726	0.5726			
	2	30	0.5726	0.5726			
	5	40	0.5708	0.5708			

Similar determinations were made with solutions of different concentrations and the results are in Table II.

TABLE II.

$[\text{HCl}] = 11.6N$ .

Cell.	$[\text{SeO}_2]$ .	$[\text{Se}]$ .	$E(20^\circ)$ .	$\Delta E$ .
A <sub>1</sub>	0.087	0.0134	+0.5501	—
A <sub>2</sub>	0.087	0.0134	0.5498	0.0222
D	0.087	0.00134	0.5720	
E	0.087	0.000134	0.5970	0.0250
B	0.0087	0.00134	0.5480	
F	0.0087	0.000134	0.5720	0.0260
C	0.00087	0.000134	0.5436	

In Cell A<sub>1</sub>, the junction  $N\text{-HCl}|\text{KCl}(\text{sat.})$  is stationary, but in A<sub>2</sub> and all the other cells the flowing junction was used.

*The Influence of Concentration of Selenium Dioxide and of Selenium on Oxidation Potential.*

(a) *Selenium*.—Table II gives this relation, since in Cells A<sub>2</sub>, D and E the  $[\text{SeO}_2] = 0.087$  is constant and  $[\text{Se}]$  undergoes tenfold changes. Cells B and F afford a similar comparison.  $\Delta E$  is the difference in *E.M.F.* for a tenfold change in  $[\text{Se}]$  and it amounts to 0.0222 to 0.0260 volt.

(b) *Selenium Dioxide*.—Table III gives this relation similarly, and it will be seen that  $\Delta E$  for a tenfold change in  $[\text{SeO}_2]$  varies from 0.0250 to 0.0284 volt.

TABLE III.

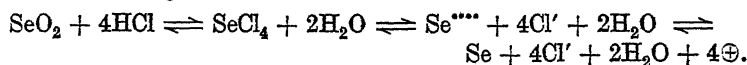
Cell.	$[\text{SeO}_2]$ .	$[\text{Se}]$ .	$E(20^\circ)$ .	$\Delta E$ .
D	0.087	0.00134	0.5720	0.0260
B	0.0087	0.00134	0.5480	
E	0.087	0.000134	0.5970	0.0250
F	0.0087	0.000134	0.5720	
C	0.00087	0.000134	0.5436	0.0284



*Mechanism of the Oxidising Action of Selenium Dioxide and of Sulphur Dioxide.*

The reduction of selenium dioxide in concentrated acid solution may conceivably proceed in a number of ways, of which the following may be considered.

1. The selenium dioxide dissolves in concentrated acid to form selenium tetrachloride, which ionises into quadrivalent selenium ions,  $\text{Se}^{++++}$ . On reduction, the four positive charges are removed and elementary selenium results:



The potential variations,  $\Delta E$ , would be given by  $\Delta E = 0.058/4 \cdot \log [\text{Se}]/[\text{SeO}_2]$ , and for a tenfold change in  $[\text{Se}]$  or in  $[\text{SeO}_2]$ ,  $\Delta E = 0.058/4 = 0.0145$  volt.

2. The reduction does not proceed entirely from the quadrivalent state down to elementary selenium, but only through certain intermediate stages, for example, from quadrivalent to bivalent selenium. The essential portion of such a process may be represented



whence  $\Delta E = 0.058/2 \cdot \log [\text{Se}^{++}]/[\text{Se}^{++++}] = 0.058/2 \cdot \log [\text{Se}]/[\text{SeO}_2]$ , and for a tenfold change in  $[\text{Se}]$  or in  $[\text{SeO}_2]$ ,  $\Delta E = 0.058/2 = 0.029$  volt.

Since part of the selenium dioxide is used in dissolving the selenium, the effective concentration is actually less than  $[\text{SeO}_2]$  and a value somewhat smaller than 0.029 for  $\Delta E$  will be obtained.

The existence of derivatives of bivalent selenium is indicated by the solubility of selenium in strong acid solutions containing selenium dioxide:  $\text{SeO}_2 + \text{Se} = 2\text{SeO}$ . In this connexion, it may be observed that selenium dissolves in selenic acid giving a green solution believed to contain  $\text{Se}_2\text{O}_3$ , an analogue of  $\text{SeSO}_3$  which is formed by dissolving selenium in sulphuric acid (*Chem. News*, 1889, 59, 268).

Either hypothesis depends on certain assumptions regarding the degree of ionisation and the unimolecular nature of the respective constituents in the equations. Experiments on these points are still proceeding. The experimental results for  $\Delta E$  fall between those demanded by the two theories, but are rather in favour of the second.

The hypothesis that selenium acquires positive charges and behaves as an electropositive element is reasonable, since it has certain characteristics of a metal which are exhibited by its analogue tellurium, although scarcely at all by sulphur. Nevertheless the

analogy with sulphur, even if only shown to a slight extent, is of interest in a study of the oxidising properties of sulphur dioxide and would furnish an explanation if sulphur could also become electropositive in acid solution (J., 1920, 117, 1246).

Since negatively charged selenium ions  $\text{Se}''$  or  $\text{Se}_n''$  have already been identified in alkaline solutions, the present indication of positively charged selenium ions in acid solution furnishes additional evidence of the amphoteric nature of selenium (compare Le Blanc, Reichenstein, Müller, and Abegg; references, *Z. physikal. Chem.*, 1921, 97, 257; 1922, 100, 346).

*The Effect of Light.*—The potential of one of the oxidation cells, which had been kept in darkness, was not affected by sudden exposure to direct sunlight, or to the light of four filament lamps at a distance of a foot. On the other hand, bright metallic electrodes (made by melting selenium on platinum) in hydrochloric acid solutions of selenium dioxide and selenium gave a potential which was distinctly influenced by exposure to light. The selenium rapidly lost its brightness and the photosensitiveness disappeared. A selenium electrode made by the cathodic deposition of selenium on a selenium rod, and therefore covered with a layer of the amorphous kind, was quite unaffected by light.\*

The photosensitiveness of the *E.M.F.* of selenium in aqueous solutions has been observed by Sabine and others (for references see C. Ries, "Das Selen," 1918, p. 188) and, although the significance of the presence of concentrated acid, selenium dioxide and dissolved selenium in determining the potential has not hitherto been emphasised, it is obviously of value in explaining the processes underlying many of their experiments.

These considerations are also useful in explaining the electro-metric titration of selenium solutions by the bimetallic electrode system of Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, 45, 933).

### Summary.

The system selenium dioxide-selenium in concentrated hydrochloric acid gives a reproducible oxidation potential which has been measured.

The potential is unaffected by the action of light.

The influence of concentration of selenium and of selenium dioxide on potential has been studied, the changes for tenfold dilutions corresponding to 0.022—0.028 volt.

The oxidising action of selenium dioxide is provisionally attributed

\* We are indebted to Mr. W. F. Waters for some assistance in these experiments.

to the presence of selenium tetrachloride, which yields positively charged selenium ions.

The oxidising action of selenium dioxide and of its analogue, sulphur dioxide, are compared.

We desire to express our thanks to the Department of Scientific and Industrial Research for a grant which enabled one of us (F. J.) to take part in this investigation.

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### CXXXI.—*Applications of Thallium Compounds in Organic Chemistry. Part III. Alkylations.*

By CHRISTINA MARY FEAR and ROBERT CHARLES MENZIES.

THE preparation of alkyl derivatives by heating organic thallous compounds with alkyl iodides, suggested by the resemblance between thallous and silver halides, proceeds smoothly if the thallous compound is soluble in the alkylating agent, or if, being of an amorphous nature, it presents to it a large surface, whilst sparingly soluble, well-crystallised substances enter into the reaction slowly, if at all.

Thallous palmitate, for instance, which is appreciably soluble in methyl iodide, is completely converted into methyl palmitate by boiling with this solvent for 4 hours. Again the thallous salt of ethyl acetoacetate, readily soluble in cold ethyl iodide, requires 3 hours for ethylation, and the amorphous yellow *trithallium methylglucoside*, insoluble in methyl iodide, gives, after treatment for 5 hours, a trimethyl methylglucoside in good yield. On the other hand, treatment of the well-crystallised, sparingly soluble tetrathallium tartrate with boiling methyl iodide for 100 hours gives an incompletely methylated product, whilst an attempt to methylate the thallous salt of *o*-nitrophenol had to be discontinued. The preparation of trimethyl methylglucoside from trithallium methylglucoside is interesting in view of McKenzie's suggestion (J., 1899, 75, 765) that the most plausible explanation of methylation by Purdie's silver oxide method is that an intermediate unstable silver derivative is formed which subsequently undergoes double decomposition with the alkyl halides (see also Lander, J., 1900, 77, 747; 1903, 83, 416).

The rotations observed both in this case and in that of the product of methylation of tetrathallium tartrate indicate that at any rate in these instances racemisation does not occur.

## EXPERIMENTAL.

Treatment of their thallous salts with alkyl iodides affords a useful means of preparing small quantities of the esters of higher fatty acids. Thus from 0.47 g. and 0.55 g. of thallous stearate, 0.18 g. (m. p. 38.5°; yield 62%) and 0.26 g. (m. p. 37.5°; yield 79%) of methyl stearate were obtained, respectively, after refluxing for 4 hours with methyl iodide, and recovery of excess of this solvent, by extracting the resulting mixture of methyl stearate and thallous iodide with ether (Found in the latter sample: C, 76.4; H, 12.9. Calc., C, 76.4; H, 12.8%). By using larger quantities of material and benzene as solvent, almost theoretical yields may be obtained, thus 3.24 g. (theory, 3.26 g.) of methyl stearate (m. p. 38.5°) were produced by boiling 5.33 g. of thallous stearate with methyl iodide in benzene, a quantitative yield of thallous iodide also resulting.

The smaller-scale preparations, however, illustrate a convenient technique when small quantities of the higher fatty acids are under examination, it being easy to obtain from less than 1 g. of the acid its titration value, and its ethyl or methyl ester pure and in quantity sufficient for analysis and determination of melting point. Thus 0.579 g. and 0.557 g. of palmitic acid dissolved in alcohol required respectively 7.5 c.c. and 7.0 c.c. of 0.307*N*-aqueous thallous hydroxide (calc., 7.35 c.c. and 7.0 c.c.). On evaporation of the solution resulting from the former titration and treatment of the residual dry thallous palmitate with boiling methyl iodide, 0.4 g. of methyl palmitate was obtained (yield 66%; m. p. after recrystallisation from methyl alcohol 29.5°. Found: C, 75.4; H, 13.0. Calc., C, 75.5; H, 12.7%). Evaporation to dryness before treatment with methyl iodide is essential, as, on addition of methyl iodide to the solution resulting from the second titration and boiling under reflux as before, a product was obtained which had an acid reaction and a high melting point (31.5°).

By using propyl iodide, 2 g. of *propyl palmitate* were obtained from 5 g. of thallous palmitate by boiling for 1 hour (yield 63%; m. p. 15.3—15.4°, b. p. 209°/22 mm. Found: C, 76.5; H, 12.95.  $C_{19}H_{38}O_2$  requires C, 76.4; H, 12.8%). The low yield was due to loss in manipulation.

*Ethylation of Ethyl Acetoacetate.*—A boiling solution of 23.4 g. of thallous ethyl acetoacetate (Christie and Menzies, J., 1925, 127, 2372) in ethyl iodide rapidly deposited thallous iodide as a brick-red powder which became yellow after 2 hours. After boiling for a further hour, it was filtered off from the cooled mixture (yield, 21.8 g.; calc., 23.3 g.). On fractionation, 8.6 g. of ethyl ethyl-acetoacetate (yield 77.5%), distilled between 192° and 195° (uncorr.)/

756 mm. (Found: C, 60.7; H, 9.0. Calc., C, 60.7; H, 8.9%.  $D_D^{25}$  0.9924,  $n_D^{25}$  1.4237.  $R_D$ , 40.72. Calc. for keto-form, 40.98, for enol-form, 41.92; and for the isomeric ethyl  $\beta$ -ethoxycrotonate, 42.08. Compare Lander, *loc. cit.*, p. 738).

*Trithallium methylglucoside* may be obtained in good yield as a yellow, amorphous powder by adding methylglucoside dissolved in a little water to a hot concentrated solution of thallous hydroxide. If 4 equivalents of the latter be used to each molecular equivalent of methylglucoside, the thallium content of the product approximates closely to that required for trithallium methylglucoside (Found as iodide: Tl, 76.4, 76.15.  $C_7H_{11}O_6Tl_3$  requires Tl, 76.2%). The trithallium methylglucoside used for the methylation described below was prepared from 21.6 g. of  $\alpha$ -methylglucoside (m. p. 165.5°;  $[\alpha]_D +158.8^\circ$  for a 5.2% solution in water) in 13 c.c. of water and 206 c.c. of 1.62*N*-thallous hydroxide (3 equivs.), which immediately before the addition of the methylglucoside was concentrated by boiling to about half-bulk; 76.8 g. (yield 85%) separated at once (Found as iodide: Tl, 73.8%). 36.5 G. of this product were boiled with methyl iodide for 5 hours; the reaction was then complete. The excess of methyl iodide was removed, and the residue extracted with methyl alcohol; 9.8 g. of syrup (dried in a vacuum at 100°) were obtained, the theoretical yield calculated for trimethyl methylglucoside being 10.7 g. On distillation three fractions were obtained: (1) 2.25 g., b. p. 137°/2.2 mm.; (2) 4.35 g., b. p. 136.6°/2.3 mm. to 137.2°/1.5 mm.; (3) 1 g., b. p. 140°/2.5 mm. to 164°/1.8 mm. The optical and analytical data are in the following table:

$n_D$ .	$[\alpha]_D$ in water.	$[\alpha]_D$ * in ethyl alcohol.	C %.	H %.	OMe %.
(1) 1.4569	164° (1.6%)	165.9° (0.8%)	50.4	8.65	50.4
(2) 1.4592	153.1° (1.2%)	154.6° (1.2%)	50.9	8.5	49.0
(3) 1.464					46.0
Calc. for trimethyl methylglucoside:			50.8	8.5	52.5

\* Compare Purdie and Bridgett, J., 1903, 83, 1037, and Haworth, J., 1915, 107, 13.

*Attempted Preparation of Methyl Dimethoxysuccinate.*—From 75 g. of tetrathallium tartrate, boiled under reflux with methyl iodide for approximately 100 hours, 12.5 g. of a syrup were obtained, which distilled as a homogeneous liquid, b. p. 146°/25 mm. to 146.1°/23 mm.,  $n_D$  1.4363,  $[\alpha]_D$  72.17° (Found: OMe, 50.8, 51.6. Calc. for four methoxy-groups, OMe, 60.2%; for three methoxy-groups, OMe, 48.4%). The syrup did not solidify and a nucleus of methyl dimethoxysuccinate, kindly supplied by Professor Haworth, was dissolved.

*Preparation of o-Methoxybenzaldehyde.*—From 20.2 g. of thallous

salicylaldehyde, refluxed for 50 hours with methyl iodide in benzene, after removal of unchanged thallium salicylaldehyde by agitation with aqueous sodium hydroxide and subsequent distillation in steam, 5.2 g. of *o*-methoxybenzaldehyde, m. p.  $36.3^{\circ}$  (yield 62%) were obtained (Found: OMe, 21.0. Calc., OMe, 22.8%) (compare Irvine, J., 1901, 79, 668).

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### CXXXII.—*Determination of the Rate of Hydrolysis of Sparingly Soluble Esters.*

By R. CHRISTIE SMITH and H. A. PATERSON.

THE rate of hydrolysis of esters is most conveniently determined by estimating the amount of free acid formed at successive intervals. With sparingly soluble esters this involves the use either of large quantities of ester solutions, or of smaller quantities, giving relatively larger percentage errors. The use of strong acid (or base) for hydrolysis in order to speed up the reaction and so give increased titrations, brings in its train the difficulty of accurately determining the amount of base (*e.g.*, baryta) necessary for neutralisation of the acid. A method has been evolved which minimises the above difficulties.

In the reaction equation  $dx/dt = kC$  the velocity coefficient can be interpreted as the fraction of the concentration  $C$  which is converted in the unit of time  $dt$ , and, for our purpose, it will be sufficiently accurate to define  $k$  as the fraction of the concentration  $C$  transformed in one minute. If, therefore, the solution is kept with a constant concentration  $C$  of ester, the same amount of ester will be transformed every minute. Hence it will only be necessary to keep the solution with a constant concentration of ester during a sufficiently long period to allow of a reasonable titration being obtained. The most convenient concentration is, of course, that of saturation. Hence if  $x$  c.c. of  $N$ -baryta represent the amount of ester transformed per minute in a 25 c.c. sample, the weight of ester transformed in 100 c.c. is  $0.004 Mx$  g.

In order to test the accuracy with which  $k$  could be determined by this method, propyl acetate, ethyl propionate, and propyl butyrate (see Table I), whose velocity coefficients could also be

determined in the usual way, were chosen. The results do not show such good agreement in the case of propyl acetate as of propyl butyrate, but this is ascribed to the fact that propyl acetate is more soluble, and hence diluted the aqueous layer to an abnormal extent (see below).

TABLE I.

Ester.	$k$ (homogeneous method).	$k$ (heterogeneous method).
Propyl acetate .	0.0063	0.0061
Ethyl propionate	0.0068	0.0071
Propyl butyrate.	0.0039	0.0039

TABLE II.

Ester.	$k$ (by new method).	Solubility (g. per 100 c.c.).
Benzyl acetate .	0.0051	0.234
Benzyl propionate	0.0056	0.078
Phenyl acetate .	0.0046	0.588

The velocity coefficients for the homogeneous reaction were determined in the usual manner. For the heterogeneous reaction of the substances in Table I, 250 c.c. of *N*-hydrochloric acid were shaken with an excess of the ester in a 300 c.c. ground-stoppered bottle in a rotary thermostat at 25°. At intervals, 25 c.c. of solution were withdrawn, 25 c.c. of *N*-sodium hydroxide added, and the excess of acid was titrated with baryta, the amount of ester transformed per minute being calculated from the titre. In the cases of benzyl acetate, benzyl propionate, and phenyl acetate, only 25 c.c. of *N*-hydrochloric acid were placed in the bottle, an excess of ester was added, and, after a given period in the thermostat, the whole was titrated. To ensure greater accuracy, the additions of normal acid and base were checked by weighing. The solubilities of these esters were determined by basic hydrolysis of 25 c.c. of saturated solution. The results are in Table II.

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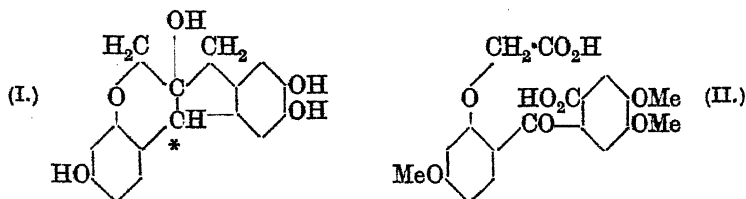
[Received, February 27th, 1926.]

CXXXIII.—*Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part I. Veratrylidene-7-methoxychromanone and an Account of a New Synthesis of some Benzopyrylium Salts.*

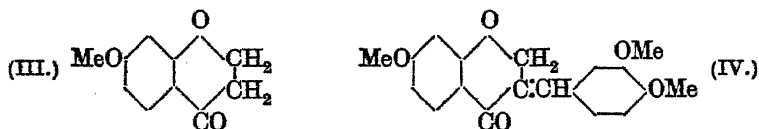
By WILLIAM HENRY PERKIN, jun., JNANENDRA NATH RÂY, and ROBERT ROBINSON.

THE investigation of brazilin and hæmatoxylin by analytical methods, commenced in 1901 (Part I, Gilbody, Perkin, and Yates, J., 79, 1401) and completed in 1909 (Part X, Perkin and Robinson, J., 95, 381), resulted in the demonstration that brazilin has the constitution (I) and that hæmatoxylin is an analogous derivative of pyrogallol. In the course of the work a number of derivatives

of brazilin and hæmatoxylin were synthesised, the more important being anhydrobrazilic acid, brazilic acid, and the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids (Perkin and Robinson). Brazilinic acid (II) is an example of a derivative containing all the carbon atoms of trimethylbrazilin, and the correctness of the carbon skeleton of (I) was further confirmed by the



synthesis of isobrazilein and of isohæmatein (Crabtree and Robinson, J., 1918, 113, 859; 1922, 121, 1033), substances which contain intact the ring-system of brazilin. There exists, however, no synthetical \* proof of the position of the hydroxyl group in (I), since the production of 3:7-dihydroxychromone, an oxidation product of brazilein (Schall and Dralle, *Ber.*, 1888, 21, 3016), could be explained in a natural manner by several brazilein formulæ and, for example, by that in which the hydroxyl is in the position denoted by an asterisk in (I). Apart from this consideration an obvious interest attaches to the synthesis of brazilin, an interest which is only heightened by the difficulty of the problem and by the probable necessity of devising new methods for its solution. In 1911, Tschitschibabin and Nikitin (*J. Russ. Phys. Chem. Soc.*, 43, 1185) published a note on 7-methoxychromanone (III), and this led two of us to submit a preliminary note (P., 1912, 28, 7) on the experiments which had been made on the same subject with the object of synthesising trimethylbrazilin.

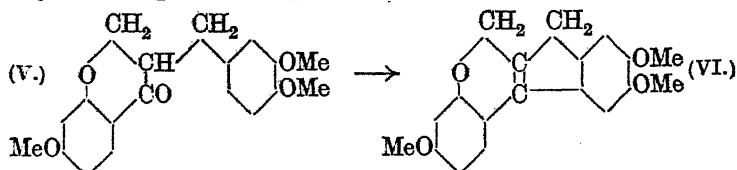


3-Veratrylidene-7-methoxychromanone (IV), m. p. 140°, was described in the note of 1912 and comment was made on its close relationship to trimethylbrazilin. Pfeiffer and Grimmer (*Ber.*, 1917, 50, 911) then announced their intention of attacking the problem of the synthesis of brazilin and its derivatives and selected the method indicated in the above-mentioned note of 1912. These

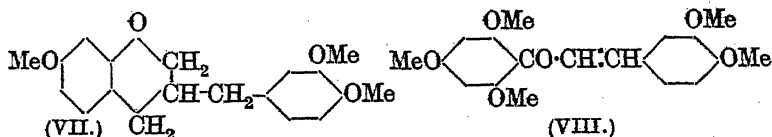
\* The position assigned to the hydroxyl in (I) is indicated by the fact that tetramethyldihydrobrazileinol yields trimethylbrazilone on oxidation (Engels, Perkin, and Robinson, J., 1908, 83, 1130).



authors reported the preparation of anisylidene-7-methoxychromanone, and in consequence the fact that a nearer relative of brazilin, namely, veratrylidene-7-methoxychromanone, had been prepared was pointed out in a footnote to a paper in this *Journal* (1918, 113, 859). Undeterred by this, Pfeiffer and Emmer (*Ber.*, 1920, 53, 945) proceeded to the preparation of veratrylidene-7-methoxychromanone, m. p. 140°, and stated that they had succeeded in reducing the substance to a dihydro-derivative (V) by means of hydrogen in the presence of platinum black.



The experiments on this subject, interrupted at the time because of other interests, have now been resumed, and in this communication we bring together some observations arising out of work as yet unfinished. The preparation of (V) was one of the primary objects of the investigation, since dehydration to (VI) should be feasible. We are, however, of the opinion, for various reasons, that the product of the catalytic \* hydrogenation of veratrylidene-7-methoxychromanone is 3-homoveratryl-7-methoxychroman (VII) and not the ketone (V) as suggested by Pfeiffer and Emmer (*loc. cit.*).

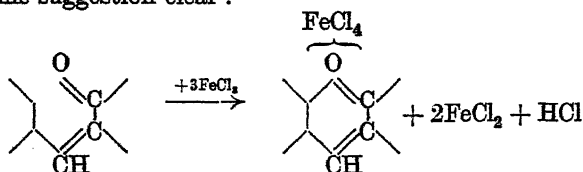


This result is by no means unique, since Freudenberg (*Ber.*, 1920, 53, 1416) has shown that the pentamethoxychalkone (VIII) is reduced to the related diphenylpropane derivative by hydrogen in presence of spongy platinum.

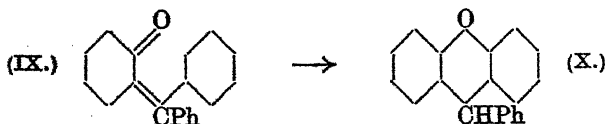
Further attempts to reduce veratrylidene-7-methoxychromanone to a dihydro-derivative will be made. Our objects in making certain further experiments are explained in the sequel (pp. 947, 948, 950). In the presence of acid condensing agents veratrylidene-7-methoxychromanone (IV) might be expected to undergo internal condensation with formation of isobrazilein salts, readily recognisable on account of the intense green fluorescence which they exhibit. Under several sets of conditions it was, in fact, noticed that substances exhibiting intense green fluorescence could be derived from

\* We employed palladium as the catalyst, but it should be noted that platinum is usually regarded as even more efficient.

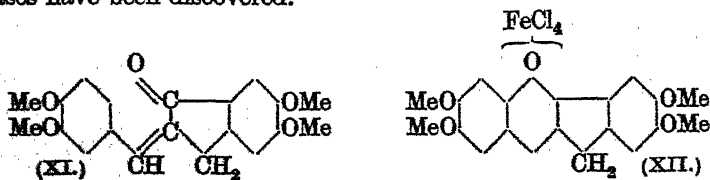
veratrylidene-7-methoxychromanone. The yield was usually very small, but when the unsaturated ketone was dissolved in acetic anhydride and anhydrous ferric chloride added, a relatively considerable amount of an oxonium ferrichloride was produced. The new salt was readily purified and exhibited an even more striking fluorescence than isobrazilein chloride trimethyl ether. It has the composition  $C_{19}H_{15}O_5Cl_4Fe$  and is therefore derived from veratrylidene-7-methoxychromanone,  $C_{19}H_{16}O_5$ , by some process of oxidation. In considering this matter it seemed possible that the pyrylium ring, which the salt obviously contained, might be produced, not by modification of the heterocyclic system already present, but by attachment of the oxygen of the carbonyl group to carbon of the veratrole nucleus. The following partial formulæ will serve to make this suggestion clear:



Such a reaction, leading to the formation of a benzopyrylium salt, has not been previously observed, but it is similar, both in principle and in method, to Diltz's synthesis of pyrylium salts (*J. pr. Chem.*, 1916, 94, 53) and it also resembles many methods of preparation of oxazine, thiazine and azine dyestuffs. The simplest analogy is furnished by an observation recently made by Gomberg and Nishida (*J. Amer. Chem. Soc.*, 1923, 45, 190): *o*-hydroxy-triphenylcarbinol in solution above  $100^\circ$  yields 9-phenylxanthane (X), no doubt through the intermediate (IX).



We found support for this view of the reaction in the fact that veratrylidene-5:6-dimethoxyhydrindone (XI) could be similarly oxidised to an oxonium ferrichloride (XII), and several further cases have been discovered.



The process is nevertheless not a very general one and up to the present we have only found it to succeed with the veratrylidene, *o*-veratrylidene or piperonylidene derivatives of cyclic ketones. Thus veratrylideneacetoveratrone and *m*- or *p*-methoxybenzylidene-5:6-dimethoxyhydrindone gave negative results.

#### EXPERIMENTAL.

*m*-Methoxyphenol.—The conditions for the semi-methylation of resorcinol have been studied and the following process has been devised. Potassium hydroxide (40 g.) dissolved in water (100 c.c.) was gradually added to a mixture of resorcinol (110 g.), alcohol (100 c.c.), and methyl sulphate (120 c.c.), which was frequently shaken and cooled in running water. An hour afterwards, an equal quantity of aqueous potassium hydroxide was gradually introduced and finally the mixture was heated on the steam-bath for 45 minutes. The solution was then acidified, extracted with benzene and the separated benzene layer was washed with aqueous sodium hydroxide until nothing more was removed. The alkaline solutions were acidified and again extracted with benzene. This process removes unchanged resorcinol and resorcinol dimethyl ether may be recovered from the first benzene solution. The second benzene extract was dried and distilled, 50 g., b. p. 240–242°, being obtained.

$\beta$ -*m*-Methoxyphenoxypropionic Acid.—This substance was originally obtained from *m*-methoxyphenol in aqueous alkaline solution by interaction with  $\beta$ -iodopropionic acid. The use of  $\beta$ -bromopropionic acid results in rather improved yields, but  $\beta$ -chloropropionic acid is still better. A solution of  $\beta$ -chloropropionic acid (60 g.) in water (225 c.c.) and sodium bicarbonate (45.3 g.) was mixed with one of *m*-methoxyphenol (67.5 g.) in aqueous potassium hydroxide (100 c.c. of 30%), and the liquid heated on the steam-bath for 3 hours. After acidification, the mixture was extracted with ether, and the acid removed from the extract by means of aqueous sodium bicarbonate.  $\beta$ -*m*-Methoxyphenoxypropionic acid (30 g.) and recovered *m*-methoxyphenol (28–30 g.) were ultimately isolated.

We refrain from detailed descriptions of the substances mentioned in the note of 1912 (*loc cit.*), the properties of which have since been placed on record by Pfeiffer and his colleagues.

*m*- $\beta$ -Hydroxyethoxyanisole, b. p. 290°/15 mm., was prepared from *m*-methoxyphenol, sodium ethoxide, and ethylene chlorohydrin in alcoholic solution. In an attempt to replace the hydroxyl group in this substance by bromine with the ultimate object of preparing  $\beta$ -*m*-methoxyphenoxypropionitrile, a curious result was

obtained. The glycol ether (11 g.) was dissolved in benzene and phosphorus tribromide (20 g.) added, causing a copious evolution of hydrogen bromide. The mixture was gently heated in the steam-bath for 2 hours, and the neutral product isolated. This was dissolved in alcohol, and the solution boiled for 3 hours after the introduction of a concentrated aqueous solution of potassium cyanide (5 g.). On addition of water, a solid (6 g.) was precipitated and the substance crystallised from alcohol in long, colourless needles, m. p. 65° (Found: C, 70.1; H, 6.6.  $C_{16}H_{18}O_4$  requires C, 70.1; H, 6.5%). The substance appears to be the ethylene ether of *m*-methoxyphenol,  $MeO \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_6H_4 \cdot OMe$ .

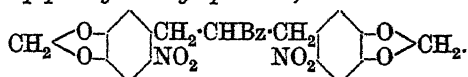
7-Methoxychromanone (III) has been prepared by several methods but, although it is not satisfactory, the original process of dehydration of methoxyphenoxypropionic acid in benzene solution by means of phosphoric anhydride is still the best. Phosphoric anhydride (80–90 g.) was gradually added to a gently boiling solution of methoxyphenoxypropionic acid (30 g.) in benzene (200 c.c.). After heating for 4 hours, the neutral ketone was isolated and purified by distillation. The yield was 6–8 g., b. p. 197°/30 mm., m. p. 56° after crystallisation from light petroleum. The semicarbazone separates from alcohol in glistening plates, m. p. 222° (decomp.).

3-Veratrylidene-7-methoxychromanone (IV).—This substance was at first prepared by condensation of 7-methoxychromanone and veratraldehyde in methyl-alcoholic solution in presence of potassium hydroxide, but the following is a much improved method. A rapid stream of hydrogen chloride was passed for one hour through a solution of methoxychromanone (5 g.) and veratraldehyde (5 g.) in acetic acid (10 c.c.) cooled in a freezing mixture. Next day the deep red solution was filled with a red crystalline mass of the *hydrochloride* of the unsaturated ketone and this was collected and decomposed with crushed ice. The substance was finally crystallised from much methyl alcohol, separating in colourless needles, m. p. 141°. The yield was 5.6 g.

3-Homoveratryl-7-methoxychromanone (VII).—A solution of veratrylidene-7-methoxychromanone (7 g.) in acetic acid (200 c.c.) was mixed with aqueous palladous chloride (30 c.c. of 1%) and agitated in an atmosphere of hydrogen until absorption of the gas slackened. The temperature was then raised to 50–60° and the agitation in hydrogen continued for about 6 hours. Most of the acetic acid was removed from the filtered solution by distillation under diminished pressure, and the residue neutralised with aqueous sodium carbonate. The colourless solid which was precipitated was collected and when once crystallised from methyl alcohol had m. p. 89°. This is the m. p. assigned by Pfeiffer and Emmer (*loc. cit.*)

to the supposed ketonic product of the catalytic hydrogenation of veratrylidene-methoxychromanone. After three or four successive crystallisations from methyl alcohol or from aqueous acetone, the substance is obtained in slender, colourless needles, m. p. 96—97° (Found: C, 72.2; H, 7.2.  $C_{19}H_{22}O_4$  requires C, 72.6; H, 7.0%). The substance dissolves in sulphuric acid to a pale rose solution and is inactive towards reagents for the carbonyl group. We do not go so far as to assert that the products of the hydrogenation of veratrylidene-methoxychromanone in presence of platinum (Pfeiffer and Emmer) and of palladium are identical, although we think it probable that this will prove to be the case.\* We have not been able to isolate any product of the reduction other than that here described and it is noteworthy that, whereas the semicarbazone of the reduction product of anisylidene-methoxychromanone was described (Pfeiffer and Emmer, *loc. cit.*), no proof, other than analysis, was offered of the ketonic nature of the reduction product, m. p. 89°, of veratrylidene-methoxychromanone.

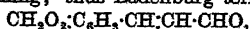
*Di- $\omega$ -6-nitropiperonylisobutyrophenone,*



—Attempts are in progress to introduce the homoveratryl group into 7-methoxychromanone by a direct process and preliminary experiments on the interaction of the sodium derivative of acetophenone and homopiperonyl † bromide have been made. Powdered sodamide (2 g.) was added to acetophenone (6 c.c.) dissolved in dry ether (75 c.c.) and, after the mixture had been occasionally shaken during an hour, homopiperonyl bromide (11 g.) was added to the clear solution. The mixture was heated on the steam-bath for 1 hour, water was added, and ether and acetophenone were removed in

\* It would be anticipated that the m. p. of a chromanone should be higher than that of the related chroman.

† Possibly on account of its close relation to piperonal the alcohol  $CH_2O_2:C_6H_5\cdot CH_2\cdot OH$  has been called piperonyl alcohol, and consequently the amine,  $CH_2O_2:C_6H_5\cdot CH_2\cdot CH_2\cdot NH_2$ , has been named homopiperonylamine. This nomenclature is, however, erroneous and its continuance must necessarily create confusion. The historical case for regarding the group  $CH_2O_2:C_6H_5\cdot$  as piperonyl is overwhelming; thus Ladenburg termed



piperonylacrolein and the words piperonyl, veratryl, and anisyl have been very widely employed to indicate the corresponding substituted phenyl groups. The compound often called piperonyl alcohol is really homopiperonyl alcohol and the base for which the usual name is homopiperonylamine is best termed  $\beta$ -piperonylethylamine. It is obviously undesirable to employ one and the same word to denote two different radicals (compare Robinson and Robinson, J., 1914, 105, 1461; Oberlin, *Arch. Pharm.*, 1925, 9, 10).

a current of steam. The residual yellow oil could not be crystallised but, on nitration in acetic acid solution, it yielded a compound which crystallised from benzene in needles, m. p.  $193^{\circ}$  with sintering at  $175^{\circ}$  (Found: C, 51.5; H, 3.5.  $C_{16}H_{13}O_8N_3$  requires C, 51.2; H, 3.5%). The substance appears to be *dinitrodihomopiperonylamine*,  $CH_2O_2:C_6H_2(NO_2)\cdot CH_2\cdot NH\cdot CH_2\cdot C_6H_2(NO_2):O_2CH_2$ , obtained from homopiperonyl bromide and ammonia followed by nitration. The experiment was therefore repeated under the same conditions with the single exception that ammonia was removed from the ethereal solution by means of a current of nitrogen before introduction of the homopiperonyl bromide. In this case also the product was an oil which gave a nitro-derivative, crystallising from benzene in slender needles, m. p.  $160-161^{\circ}$  (Found: C, 60.4, 60.3; H, 3.9, 4.0; N, 6.0.  $C_{24}H_{18}O_9N_2$  requires C, 60.3; H, 3.8; N, 5.9%). The composition of this substance is in agreement with the hypothesis that it is the ketone figured at the head of this section. We have not yet completed our experiments on the homoveratrylation of methoxychromanone, but it may be mentioned that in the course of the preparation of homoveratryl alcohol a further case of the production of a derivative of cinnamic acid in a Cannizzaro reaction, carried out in the presence of ethyl alcohol, has been observed (compare Perkin and Stoyle, J., 1923, 123, 3174). Potassium hydroxide (30 g.) dissolved in ethyl alcohol (75 c.c. of 98%) was added to veratraldehyde (20 g.) dissolved in the same solvent (25 c.c.). Next day, the crystals which had separated were collected and found to consist of potassium 3:4-dimethoxycinnamate and to yield 7.8 g. of the corresponding acid. Veratric acid and homoveratryl alcohol were isolated from the filtrate in the usual manner.

*2-Bromo-5:6-dimethoxy-1-hydrindone*,  $C_6H_2(OMe)_2\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}CHBr$ .

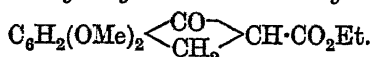
—A portion (18 c.c.) of a solution of bromine (1 c.c.) in carbon tetrachloride (20 c.c.) was gradually added to 5:6-dimethoxyhydrindone (3.0 g.) dissolved in warm carbon tetrachloride (30 c.c.). After 1 hour the thick paste that had been produced (3.0 g.) was washed with carbon tetrachloride; it crystallised from alcohol in very pale yellow, rectangular plates, m. p.  $157^{\circ}$  (Found: Br, 28.3.  $C_{11}H_{11}O_3Br$  requires Br, 29.5%).

*2-Cyano-5:6-dimethoxy-1-hydrindone*,  $C_6H_2(OMe)_2\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix}CH\cdot CN$ .

—This substance was prepared in order to attempt the synthesis of a coumarin derivative by condensation with resorcinol. Such a substance would be closely related to trimethylbrazilin. A mixture of 2-bromo-5:6-dimethoxy-1-hydrindone (3 g.), alcohol (40 c.c. of 95%), potassium cyanide (1.5 g.), and water (20 c.c.) was boiled

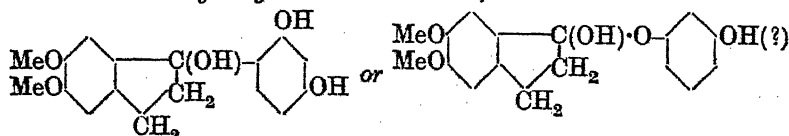
under reflux for 3 hours, then cooled, acidified with acetic acid, and extracted with ether. The residue left after removal of the solvent from the extract crystallised from alcohol in clusters of radiating needles (1—1.5 g.), m. p. 174° (Found: C, 66.1; H, 4.8.  $C_{12}H_{11}O_3N$  requires C, 66.3; H, 5.0%). The substance dissolves in dilute aqueous potassium hydroxide to a very pale yellow solution and gives no coloration with alcoholic ferric chloride. On hydrolysis with boiling 50% sulphuric acid, 5:6-dimethoxyhydrindone, identified by conversion into its piperonylidene derivative, m. p. 245°, was obtained. In a subsequent experiment, the proportion of water employed was reduced, and in this case, in addition to the above-described nitrile, a polymeric modification or condensation product of it was obtained. Bromo-5:6-dimethoxyhydrindone (10 g.), absolute alcohol (60 c.c.), potassium cyanide (3.5 g.), and water (5 c.c.) were mixed and then boiled under reflux for 2 hours, water (10 c.c.) being gradually introduced during this period. The product was added to water, and the solid (5 g.) collected. On acidification the filtrate gave 1.5 g. of the normal nitrile. The main product was sparingly soluble in most organic solvents and crystallised from glacial acetic acid in needles, m. p. 256—257° to a red liquid (Found: C, 66.4; H, 5.4%). The substance is insoluble in dilute aqueous potassium hydroxide.

*Ethyl 5:6-Dimethoxy-1-hydrindone-2-carboxylate,*



—A solution of the nitrile, m. p. 174°, described in the last section, in 20 times its weight of absolute alcohol was saturated with hydrogen chloride at the ordinary temperature for 3 hours, then boiled for 10 minutes and added to ice-cold water. The solid which separated crystallised from alcohol in colourless needles, m. p. 138° (decomp.) (Found: C, 63.9; H, 6.3.  $C_{14}H_{16}O_5$  requires C, 63.6; H, 6.1%). This ester gives with ferric chloride in alcoholic solution a transient green and then a blue coloration. We have not yet prepared a coumarin derivative from either the nitrile or the ester by condensation with resorcinol, although a number of trials have been made.

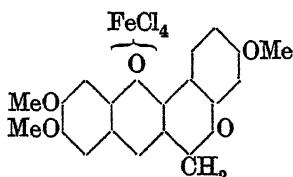
*5:6-Dimethoxy-1-hydrindone-resorcinol,*



—A solution of dimethoxyhydrindone (9.0 g.) and resorcinol (7.0 g.) in acetic acid (35 c.c.) was saturated with hydrogen chloride in the cold, kept for 1 hour, and added to water (150 c.c.). The resulting

clear liquid was neutralised with sodium carbonate; the yellow, crystalline deposit separated from boiling water in silky needles, m. p.  $78^{\circ}$  (Found: C, 67.9; H, 6.0.  $C_{17}H_{18}O_5$  requires C, 67.6; H, 5.9%). A small quantity of a yellow oil was separated in the above process on account of its sparing solubility in hot water. This consists of a substance which crystallises from methyl alcohol in needles, m. p.  $227^{\circ}$ . The by-product has not yet been further examined, nor has the compound, m. p.  $78^{\circ}$ , been characterised by the preparation of derivatives. It is remarkably sensitive to alkalis, being quantitatively resolved into its components, namely, dimethoxyhydrindone and resorcinol, by means of cold aqueous sodium hydroxide. Attempts to prepare an indene derivative by dehydration of this substance were fruitless. It is not a mere molecular compound, since it is not obtained in the absence of a condensing agent.

2:3-[7-Methoxychromeno (4:3)]-6:7-dimethoxybenzopyrylium Ferrichloride,



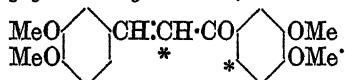
—Anhydrous ferric chloride (5.0 g.) was added to a solution of veratrylidene-7-methoxychromanone (1.0 g.) in acetic anhydride (25 c.c.) and when the reaction had subsided a further quantity of ferric chloride (3.0 g.) was added. After 10 minutes, the product was added to water (250 c.c.), and a ferrichloride precipitated by addition of a concentrated solution of ferric chloride in hydrochloric acid. The substance (yield almost quantitative) crystallised from acetic acid in crimson, prismatic needles, m. p.  $213^{\circ}$ , exhibiting a blue reflex (Found: C, 43.7, 43.4; H, 3.5, 3.2.  $C_{19}H_{15}O_5Cl_4Fe$  requires C, 43.6; H, 3.3%). Solutions of this salt in all solvents and particularly those in alcohol and acetic acid exhibit an extraordinarily brilliant greenish-yellow fluorescence. The salt is very sparingly soluble in acetic acid and more readily soluble in hot formic acid.

2-m-Methoxybenzylidene-5:6-dimethoxy-1-hydrindone.—This compound was obtained by condensation of dimethoxyhydrindone and m-methoxybenzaldehyde in hot alcoholic solution containing a few drops of concentrated aqueous potassium hydroxide. The yield was practically quantitative and the sparingly soluble substance crystallised from ethyl acetate in pale yellow needles, m. p.  $164-165^{\circ}$  (Found: C, 73.6; H, 5.7.  $C_{19}H_{18}O_4$  requires C, 73.5; H, 5.8%).



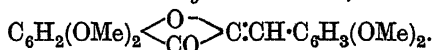
Neither this substance nor the isomeric anisylidenedimethoxyhydrindone could be converted into a pyrylium salt by means of ferric chloride in acetic anhydride solution.

3 : 4-Dimethoxystyryl Veratryl Ketone,



—An ethyl-alcoholic solution of equivalent quantities of veratraldehyde and acetoveratrone, together with a few drops of concentrated aqueous potassium hydroxide, was boiled for 10 minutes. The oil then precipitated by water solidified on repeated washing with cold water and aqueous alcohol. The substance crystallised from alcohol in flat, yellow prisms, m. p. 116° (Found : C, 69·3; H, 6·1.  $\text{C}_{19}\text{H}_{20}\text{O}_5$  requires C, 69·5; H, 6·1%). The compound is not changed to a pyrylium salt by the action of ferric chloride in acetic anhydride solution. This fact may be compared with the ready conversion of veratrylidenedimethoxyhydrindone into an oxonium ferrichloride by oxidation with ferric chloride. In the latter case, the carbon atoms in the asterisked positions in the above formula are connected by a methylene group.

2-Veratrylidene-4 : 6-dimethoxycoumaranone,



—A solution of equivalent quantities of veratraldehyde and 4 : 6-dimethoxycoumaranone (Sonn, *Ber.*, 1917, 50, 1265) in five times their weight of acetic acid was cooled in a freezing mixture and saturated with hydrogen chloride. The liquid was filled with a mass of deep red crystals of a hydrochloride in 1·5 hours; these were collected and decomposed by water, giving a bright yellow substance which crystallised from alcohol in needles, m. p. 175° (Found : C, 66·1; H, 4·9.  $\text{C}_{19}\text{H}_{18}\text{O}_6$  requires C, 66·6; H, 5·2%). No pyrylium salt could be isolated from the product of the action of ferric chloride and acetic anhydride on this substance.

2-Veratrylidene-1-hydrindone,  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{CH}_2 \end{array} \right\rangle \text{C} : \text{CH} \cdot \text{C}_6\text{H}_3(\text{OMe})_2$ .—

An ice-cold mixture of veratraldehyde (4·5 g.),  $\alpha$ -hydrindone (3 g.), and acetic acid (15 c.c.) was saturated with hydrogen chloride and after 3 hours the scarlet hydrochloride was collected, washed with acetic acid, and decomposed with water; the resulting yellow compound crystallised from acetic acid in prisms, m. p. 175° (Found : C, 76·6; H, 5·8.  $\text{C}_{18}\text{H}_{16}\text{O}_3$  requires C, 77·2; H, 5·7%).

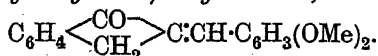
2 : 3-Indeno(1 : 2)-6 : 7-dimethoxybenzopyrylium Ferrichloride (formula similar to XII).—Anhydrous ferric chloride (15 g.) was added in portions of about 3 g. during an hour to a solution of

veratrylidene-1-hydrindone (2 g.) in acetic anhydride (35 c.c.). After 2 hours, the dark red mixture was added to a concentrated solution of ferric chloride in hydrochloric acid, and the precipitate was collected, dried, and extracted with acetic acid; the chocolate residue crystallised from absolute formic acid in brownish-red prisms, m. p. 237—238°, twinning characteristically with formation of a symmetrical cross (Found: C, 45.4; H, 3.2.  $C_{18}H_{15}O_3Cl_4Fe$  requires C, 45.5; H, 3.1%). A similar, even more sparingly soluble, ferrichloride may be obtained analogously from piperonylidene-hydrindone.

2 : 3[5 : 6-Dimethoxyindeno(1 : 2)]-6 : 7-dimethoxybenzopyrylium *Ferrichloride* (XII).—Anhydrous ferric chloride (10 g.) was gradually added to a mechanically stirred solution of 2-veratrylidene-5 : 6-dimethoxy-1-hydrindone (Perkin and Robinson, J., 1907, **91**, 1073) (3.7 g.) in acetic anhydride (50 c.c.) cooled in melting ice. After  $\frac{1}{2}$  hour, the vessel was removed from the cooling bath and a further equal quantity of sublimed ferric chloride added. After 15 minutes, the vessel was immersed in water at 40—50° and stirring continued for 20 minutes. Next day, decomposition with aqueous hydro-ferrichloric acid gave a gelatinous precipitate, which was collected and became crystalline on boiling with acetic acid. The substance crystallised from formic acid in deep brownish-crimson needles, m. p. 246—247°, with bluish-green reflex (Found: C, 45.0; H, 3.7.  $C_{20}H_{19}O_5Cl_4Fe$  requires C, 44.9; H, 3.6%). Solutions of this salt in alcohol or formic acid exhibit a phenomenal, greenish-yellow fluorescence. The substance is insoluble in cold acetic acid and sparingly soluble in formic acid.

2 : 3[5 : 6-Dimethoxyindeno(1 : 2)]-6 : 7-methylenedioxybenzopyrylium *Ferrichloride* (formula similar to XII).—Anhydrous ferric chloride (20 g.) was gradually added to a stirred solution of 2-piperonylidene-5 : 6-dimethoxy-1-hydrindone (3.5 g.) in acetic anhydride (50 c.c.) during 2 hours. The product, isolated in the usual manner, was extracted by acetic acid and crystallised from formic acid in hæmatite-red, microscopic prisms, m. p. 270° (decomp.) (Found: C, 43.6; H, 3.0.  $C_{19}H_{15}O_5Cl_4Fe$  requires C, 43.8; H, 2.9%). This very sparingly soluble substance exhibits a vivid greenish-yellow fluorescence in formic acid solution.

2-(2 : 3-Dimethoxybenzylidene)-1-hydrindone,

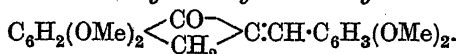


—This substance was obtained in almost theoretical yield by the methylation of 2-hydroxy-3-methoxybenzylidenehydrindone (Lawson and Robinson, J., 1924, **125**, 207) by means of methyl sulphate and potassium hydroxide in alcoholic solution. It crystallises from

alcohol in pale yellow prisms, m. p. 124° (Found: C, 77·2; H, 5·3.  $C_{18}H_{16}O_3$  requires C, 77·2; H, 5·7%).

2 : 3-Indeno(1 : 2)-5 : 6-dimethoxybenzopyrylium Ferrichloride (formula after XII).—Anhydrous ferric chloride (18 g.) was gradually added to a stirred solution of 2 : 3-dimethoxybenzylidenehydrindone (3 g.) in acetic anhydride (40 c.c.) during 1·5 hours. The product, isolated in the usual manner, crystallised from acetic acid in crimson leaflets or flat needles, m. p. 168° (Found: C, 45·2; H, 3·3.  $C_{18}H_{15}O_3Cl_4Fe$  requires C, 45·5; H, 3·1%). This salt does not exhibit strong fluorescence in any solution. *o*-Veratrylidenehydrindone might have given indeno-8-methoxybenzopyrylium ferrichloride, m. p. 187° (Lawson and Robinson, *loc. cit.*), by hydrolysis of the *o*-situated methoxyl group, but a mixture of the salts, m. p. 168° and 187°, melted indefinitely at about 140°.

2' : 3' : 5 : 6-Tetramethoxy-2-benzylidene-1-hydrindone,



—The coppery-red potassium salt, resulting from the condensation of *o*-vanillin and 5 : 6-dimethoxyhydrindone in alcoholic solution in presence of potassium hydroxide, was methylated by means of methyl sulphate. The product crystallised in glistening yellow leaflets, m. p. 183—184°, from ethyl acetate-methyl alcohol (Found: C, 70·5; H, 5·2.  $C_{20}H_{20}O_5$  requires C, 70·8; H, 5·6%). Anhydrous ferric chloride and acetic anhydride convert this substance into a ferrichloride crystallising from formic acid in brick-red leaflets, m. p. 211° (decomp.). The m. p. of the salt described below is depressed by admixture with this compound, and the salt, m. p. 211°, is therefore, in all probability, 2 : 3[5 : 6-dimethoxyindeno(1 : 2)]-5 : 6-dimethoxybenzopyrylium ferrichloride.

2 : 3[5 : 6-Dimethoxyindeno(1 : 2)]-8-methoxybenzopyrylium Ferrichloride (formula after XII).—A solution of equivalent quantities of *o*-vanillin and 5 : 6-dimethoxyhydrindone in acetic acid was saturated with hydrogen chloride for 2 hours; it was then diluted with water and a ferrichloride precipitated. The latter crystallised from much acetic acid in brownish-red needles, m. p. 250° (decomp.) (Found: C, 45·1; H, 3·6.  $C_{19}H_{17}O_4Cl_4Fe$  requires C, 45·0; H, 3·3%). Solutions of this salt do not exhibit fluorescence.

We wish to thank the Chemical Society for a grant which has defrayed a part of the expense of this investigation.

THE UNIVERSITIES OF OXFORD AND MANCHESTER.

[Received, January 14th, 1926.]

## NOTES.

*Acetyl-o-phenylenediamine and Acetyl-1:2:3-benztriazole.* By

FRANK BELL and JOSEPH KENYON.

THE cumbrous procedure for the preparation of acetyl-*o*-phenylenediamine described by Leuchs (*Ber.*, 1907, **40**, 1085) can with advantage be replaced by the following simplified method. Aluminium amalgam is added to a solution of *o*-nitroacetanilide in moist ether until the yellow colour of the solution is discharged. Owing to its limited solubility in ether, acetyl-*o*-phenylenediamine separates from the solution along with aluminium hydroxide, from which it is extracted by means of boiling benzene. It separates from benzene in small, lustrous plates, m. p. 132°.

On addition of the calculated amount of sodium nitrite to a solution of this compound in hydrochloric acid, there is produced an immediate precipitate of acetyl-1:2:3-benztriazole, which crystallises from alcohol in compact needles, m. p. 51° (Found: CH<sub>3</sub>·CO, 26·7. C<sub>8</sub>H<sub>7</sub>ON<sub>3</sub> requires CH<sub>3</sub>·CO, 26·7%). Acetyl-1:2:3-benztriazole is hydrolysed with extreme ease to give 1:2:3-benztriazole (m. p. 98°), which on acetylation reforms the acetyl derivative of m. p. 51°.—BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, February 23rd, 1926.*]

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*Density of Boric Oxide from a Fractional Crystallisation of Boric Acid.* By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and GEORGE EDWARD STEPHENSON.

A PREVIOUS communication (Briscoe, Robinson, and Stephenson, *J.*, 1925, **127**, 155) described a systematic fractional crystallisation of boric acid, involving about 1150 crystallisations. As the analytical method then applied proved useless to detect any differences in the atomic weight of boron resulting from this treatment, two end-fractions of boric acid which were still available were converted into boric oxide glass and the densities of these samples were compared by the flotation method recently described (*idem*, this vol., p. 70). The flotation liquid was the mixture of pentachloroethane and trimethylene bromide previously used having  $d_{4}^{27.00}$  1.79773 and  $d_{4}^{28.45}$  1.79372.

The data and results are as follows :

Origin of Sample.	Flotation Temp.	Density.	Relative Atomic weight.
Head Fraction Series B .....	18.18°	1.79415	10.790
Tail Fraction Series B .....	19.00	1.79445	10.796

In these determinations, the beads of each sample showed rather greater variations in density among themselves than did those derived from the various mineral sources (except sample No. 6) described in the previous communication. Therefore the authors attach little value to the third decimal figure in the present results and consider that these simply serve to indicate, in consonance with the results of a previous investigation on bromine (Robinson and Briscoe, J., 1925, 127, 138), that fractional crystallisation of boric acid has produced no change as great as 0.01 in the atomic weight of boron.

The authors desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of them (G. E. S.) to take part in this work.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, March 12th, 1926.*]

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*A Synthesis of 1 : 2-Dihydroquinaldine. A Correction.* By  
FREDERICK ALFRED MASON.

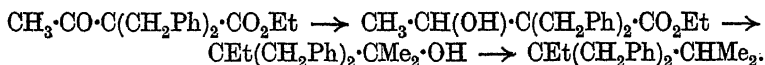
IN a previous communication (J., 1925, 127, 1032), a description was given of a synthesis of "1 : 2-dihydroquinaldine," having the properties of the substance recorded by R  th (*Ber.*, 1924, 57, 555). As subsequent work (*e.g.*, Meisenheimer and Stolz, *Ber.*, 1925, 58, 2330; K  nig and Buchheim, *ibid.*, p. 2868) has cast doubts upon the validity of some of R  th's results, a re-examination of the present author's product has been made. The melting points of the recrystallised picrates of the "1 : 2-dihydroquinaldine" and of quinaldine were carefully compared and no depression was observed on admixture, so that the product obtained by the author and described as 1 : 2-dihydroquinaldine was in fact a mixture consisting largely of quinaldine itself, and the prefix "1 : 2-dihydro" should accordingly be deleted from the title. From the results of the previous analysis, which agreed almost exactly with the theoretical figures for dihydroquinaldine (0.0882 g. gave 0.2674 g. CO<sub>2</sub> and 0.0605 g. H<sub>2</sub>O : C, 82.7; H, 7.6%. 0.1451 g. gave 12.4 c.c. N<sub>2</sub> at 18° and 754 mm. N, 9.7%) it now seems certain that the product obtained was a mixture of quinaldine and a hydrogenated substance, possibly tetrahydroquinaldine or *isobutylaniline*. This would agree with the work of Jones and Evans (J., 1911, 99, 334), who showed that the so-called "aldol base" from *p*-toluidine gave, on treatment with acids, a mixture of 2 : 6-dimethylquinoline and 2 : 6-dimethyl-tetrahydroquinoline; similar results were obtained with the "aldol base" from *m*-xylydine (compare also Mills, Harris, and Lambourne, J., 1921, 119, 1924).

Owing to the small amount dealt with, attempts to separate the

mixture were unsuccessful; its exact composition can be settled only by further investigation with larger quantities of material.—  
DYSON PERRINS LABORATORY, OXFORD. [Received, March 8th, 1926.]

*The Reduction of Ethyl Dibenzylacetoacetate.* By ELLEN  
SUSAN HILL.

DIALKYL- and diaryl-substitution products of ethyl acetoacetate should, theoretically, be convertible into quaternary hydrocarbons by well-known general reactions; ethyl dibenzylacetoacetate, for example, might be transformed into ethylisopropyldibenzylmethane:



Many attempts to carry out the first of these stages have been made; an alcoholic solution of the ester was treated with sodium, sodium amalgam, zinc and acids, hydrogen and colloidal platinum, amalgamated zinc and acids; and the ester was treated with sodium and amyl alcohol, but the only products isolated were the unchanged substance and an acid, m. p. 89° (see below). The ester was also unattacked by phosphorus pentachloride and therefore could not be reduced indirectly through the dichloro-derivative. Its stability under the conditions noted suggests steric hindrance.

By the action of sodium (twenty times the theoretical) on an ethereal solution of the ester floating on sodium hydroxide solution, two additional products were isolated. One of these was a neutral oil distilling at about 290° and probably dibenzylacetone (C, 84·6; H, 7·2; *M*, 212.  $\text{C}_{17}\text{H}_{18}\text{O}$  requires C, 85·7; H, 7·4%; *M*, 238), and the other an acid, crystallising from light petroleum, melting at 152—153° and probably hydroxyethyldibenzylacetic acid (Found: Ag, 27·6.  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{Ag}$  requires Ag, 27·6%). The yields were so small that the compounds were not fully identified.

In attempting to prepare ethyl dibenzylacetoacetate (m. p. 57°) by the action of benzyl chloride on a methyl-alcoholic solution of sodium methoxide an ester melting at 41° was obtained. This was proved to be *methyl dibenzylacetate* by preparing it from dibenzylacetic acid (m. p. 89°) and methyl alcohol. The acid (m. p. 89°) obtained by the hydrolysis of ethyl dibenzylacetoacetate was proved to be dibenzylacetic acid; it would seem, therefore, that the compound described by Fittig and Christ as dibenzylacetoacetic acid (*Annalen*, 1892, 268, 123) is really dibenzylacetic acid.—UNIVERSITY COLLEGE, NOTTINGHAM. [Received, January 21st, 1926.]

*Synthesis of Naphthathioxins.* By REGINALD CHILD and SAMUEL SMILES.

LESSER and GAD have recently described (*Ber.*, 1925, 58, 2557) experiments on the synthesis of  $\alpha\beta'$ -naphthathioxin; the present note gives the results of experiments made previously with a similar object. Di- $\beta$ -naphthyl ether when heated with sulphur and a trace of iodine at 280° for 3 hours, or when treated with sulphur chloride and aluminium chloride, gave small quantities of  $\alpha\alpha'$ -naphthathioxin (m. p. 165°), which was isolated by means of the picrate. On the other hand, in accordance with the experience of Lesser and Gad, attempts to obtain  $\alpha\beta'$ -naphthathioxin by similar treatment of  $\alpha$ -naphthyl  $\beta$ -naphthyl ether were unsuccessful. Lesser and Gad obtained 4-chloro- $\alpha$ -naphthyl  $\beta$ -naphthyl 2:1'-sulphide by treating a mixture of  $\beta$ -naphthol and 4-chloro- $\alpha$ -naphthol with sulphur chloride; but the substance is readily obtained in quantity from the reaction of  $\beta$ -naphthol with 4-chloro- $\alpha$ -naphthyl 2-sulphur bromide, the latter substance being formed from bromine and the corresponding disulphide in carbon tetrachloride. The corresponding sulphur chloride could not be obtained, owing to the ease with which chlorine displaces sulphur from the disulphide. Treatment of the foregoing  $\alpha\beta'$ -sulphide with dehydrating agents gave a small yield of a substance (m. p. 157°) which from its properties appears to be a naphthathioxin.—KING'S COLLEGE, LONDON. [*Received, February 3rd, 1926.*]

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*Critical Temperature of Mercury.* By LEONARD ALFRED SAYCE and HENRY VINCENT AIRD BRISCOE.

APPLYING the law of Guldberg and Guye (*Z. physikal. Chem.*, 1890, 5, 374, etc.), that the critical temperature of a non-associated liquid is one and a half times its normal boiling point when both constants are expressed on the absolute scale, to the case of mercury, we should conclude that its critical temperature is 675°. From a brief note in a paper by Traube and Teichner (*Ann. Physik*, 1904, 13, 620) it would appear, however, that this temperature is above 1000°. Further, calculation from surface tension data indicates that it is about 1550° (Journeau, *Bull. Soc. chim.*, 1924, 35, 1293). This figure is so widely different from that given by the Guldberg and Guye law that it seemed advisable to make a further attempt to measure the critical temperature experimentally.

For this purpose, pure redistilled mercury was enclosed in a capillary tube of transparent silica having a bore of 2 mm. and walls 3 mm. in thickness. One end of the tube was sealed off, and

the other was attached to "Hyvac" and mercury diffusion pumps while the mercury was boiled and recondensed several times to free it from dissolved gases. Finally, a portion of the tube 4 cm. long was sealed off, containing a column of mercury 1 cm. long. This silica "bomb" was supported vertically in the middle of a horizontal iron pipe 30 cm. long and 5 cm. in internal diameter, which was heated electrically by a winding of "nichrome" wire. The ends of the pipe were shielded by plate-glass and the bomb was closely observed by means of a telescope. At a temperature above  $1000^{\circ}$ , the bomb burst. Immediately before this occurred, the mercury, although at a bright red heat, was still liquid, the contrast being quite distinct between the opaque liquid and the perfectly transparent vapour.

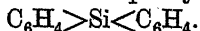
In view of the above, the experimental determination of the critical temperature of mercury would seem to be a matter of great difficulty. It is suggested, however, that mercury might be enclosed in a very stout-walled silica vessel of considerable size and heated inductively to its critical temperature by high-frequency oscillatory currents circulating in its vicinity. It might thus be possible to heat the mercury to the critical temperature while the silica vessel was so far cooled by radiation and conduction that its strength would be maintained.

We desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of us (L. A. S.) to take part in this work.—ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [Received, February 4th, 1926.]

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*Some Organo-silicon Compounds.* By RONALD RUMSEY  
WIDDOWSON.

OF certain organo-silicon compounds described by Hart (*Rep. Brit. Assoc.*, 1887, 661), one, obtained by the action of sodium on a mixture of ethylene dibromide and silicon tetrachloride, is called dichlorosilicoethylene dibromide,  $(\text{CH}_2\text{Br}\cdot\text{CH}_2)_2\text{SiCl}_2$ ; another, produced from trimethylene dibromide in a similar manner, is described as trimethylenesilicon dichloride,  $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{SiCl}_2$ , and its product of hydrolysis as trimethylenesilicon oxide. A dark brown solid, obtained from a mixture of silicon tetrachloride and *o*-dichlorobenzene, is named di-*o*-diphenylenesilicium,



Although the evidence offered in the paper is by no means convincing, the "compounds" there described are recorded in Beilstein's "Handbuch."



At Professor Kipping's suggestion and under his supervision, the author has repeated very carefully some of Hart's experiments under the same conditions. From ethylene dibromide and from *o*-dichlorobenzene no silicon compounds were formed in appreciable quantities; experiments with trimethylene dibromide were not made. These facts, a study of Hart's paper, and the general results of recent work seem to show that the organo-silicon compounds mentioned above may with advantage be deleted from the literature (compare Bygdén, *Ber.*, 1915, 48, 1236).—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 29th, 1926.*]

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*Deposition of Metallic Zinc on the Positive Pole of a Simple Voltaic Cell.* By SPENCER ROBERT HUMBY and MICHAEL WILLCOX PERRIN.

SOME observations first made in 1924 seemed to indicate that in simple voltaic cells which were left in action for some time metallic zinc was deposited on the copper plates. A large number of experiments have shown that this is the case.

Zinc and copper dipping into dilute sulphuric acid or zinc sulphate solution were connected together externally as in a simple voltaic cell; after some time the copper became covered with a layer of metallic zinc.

The following pairs of metals were treated in exactly the same way: zinc and platinum, zinc and silver, zinc and lead, zinc and iron, iron and silver, and it was found that zinc was deposited upon platinum, silver, lead, or iron, and iron upon silver. In each case, the more electropositive metal was thus deposited on the more electronegative one.

In Daniell cells, also, after short-circuiting for some days, a deposit was obtained on the copper consisting of both copper (from the copper sulphate solution) and zinc.

In the case of the simple  $\text{Zn}|\text{H}_2\text{SO}_4|\text{Cu}$  cell, zinc was deposited while the liquid in the cell was still acid. In another experiment, the liquid was stirred by bubbling hydrogen through it, but this made no difference to the results. The zinc was deposited slowly and continuously, as was shown by weighing a platinum plate at intervals during the course of the experiment. When the two poles of the cell were disconnected, the zinc was dissolved off the copper provided the solution still remained acid.

The current with a  $\text{Zn}|\text{ZnSO}_4|\text{Cu}$  cell fell to 0.006 amp. almost immediately and then more slowly to 0.0001 amp. in 30 minutes.

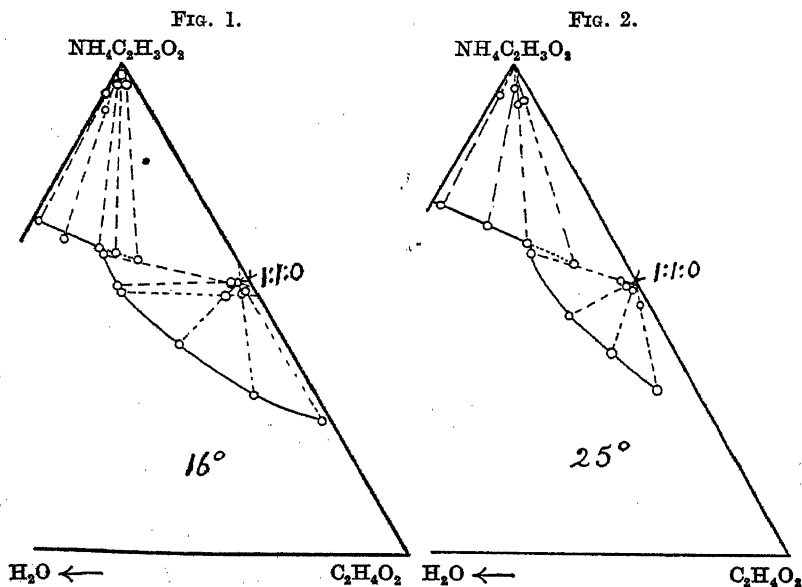
Various papers were found bearing on the subject. Odling (*Quart. J. Chem. Soc.*, 1857, 9, 289) states that in several instances

if a metal is immersed in a strong, boiling and rather acid solution of a salt of a more electropositive metal, that metal is deposited out of solution on the first, or more electronegative, metal. Raoult (*Compt. rend.*, 1873, **76**, 156) states that if pieces of gold and cadmium connected together are immersed in a boiling solution of cadmium sulphate or chloride, metallic cadmium is deposited on the gold. The gold may be replaced by copper and the cadmium by zinc or tin with the same results. Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 540) states that sodium and potassium, potassium and barium, and sodium and barium are reciprocally replaceable in their amalgams.

The results so far obtained leave no doubt as to the reality of the phenomenon, but it is hoped that additional data will shortly be ready for publication.—WINCHESTER COLLEGE and NEW COLLEGE, OXFORD. [Received, January 28th, 1926.]

*The System Ammonium Acetate-Acetic Acid-Water.* By RUTH SUGDEN.

IN addition to the acid acetate  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ,  $\text{C}_2\text{H}_4\text{O}_2$ , a hydrated complex of the composition  $2\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \cdot 3\text{C}_2\text{H}_4\text{O}_2 \cdot \text{H}_2\text{O}$  has been



described by Berthelot (*Bull. Soc. chim.*, 1864, **22**, 440). At the suggestion of Professor Rivett, isotherms of the ternary system

have been determined at 16° and 25° and a few additional measurements made at 0°. Commercial chemicals (B.D.H., A.R.) were used. Analyses of saturated solutions and wet solids were carried out by the usual ammonia distillation method, a known excess of caustic soda being used from which, by back titration, the total acetate and hence the acetic acid present could be determined. Compositions in the following table are expressed in percentages of components by weight. Water (not quoted) may be obtained by difference.

% Composition of sat. soln.		% Composition of wet solid.		% Composition of sat. soln.		% Composition of wet solid.	
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_4\text{O}_2$	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_4\text{O}_2$	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_4\text{O}_2$	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_4\text{O}_2$
Temperature 16°.							
67.8	0.91	94.4		55.6	21.7	55.3	41.3
64.4	7.73	90.9	1.46	54.3	22.7	53.0	41.6
62.6	16.0	96.6	0.96	42.5	38.1	54.6	42.8
*61.1	19.7	96.6	2.27	32.6	57.3	53.2	44.2
*59.6	23.9	96.5	2.20	27.3	72.3	53.7	44.3
61.1	17.1	55.0	41.5				
Temperature 25°.							
70.6	2.15	94.2	1.17	60.7	23.2	55.5	42.6
67.0	12.0	95.7	2.77	48.5	36.2	54.6	43.4
63.3	21.1	92.3	5.1	41.0	47.6	54.3	45.0
*58.9	31.3	92.6	5.96	33.2	59.9	51.1	47.2
Temperature 0°.							
63.8	3.7	94.5	2.38	48.9	19.6	53.6	45.7
*61.1	15.8	93.6	3.74	28.1	61.6	52.6	46.1

\* Signifies metastable.

These figures are plotted in the diagrams, from which it is seen that the existence of the complex 1 : 1 : 0 is confirmed, but that there is no evidence whatever for the existence of Berthelot's compound 2 : 3 : 1 at the temperatures examined.—UNIVERSITY OF MELBOURNE. [Received, February 8th, 1926.]

# ANNUAL GENERAL MEETING,

HELD IN THE CHEMISTRY THEATRE OF THE UNIVERSITY OF  
MANCHESTER ON THURSDAY, MARCH 25TH, 1926, AT 4 P.M.

DR. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, was in the Chair, and drew attention to the fact that this was the first occasion since the foundation of the Society in 1841 on which the Society had held its Annual General Meeting away from London.

The Report of the Council, together with the Balance Sheets and Statements of Accounts for 1925, was presented, and after a statement by the Treasurer, the adoption of the report and accounts was proposed by Prof. H. BRERETON BAKER, seconded by Dr. E. F. ARMSTRONG, and carried unanimously.

## REPORT OF COUNCIL, 1925-1926.

### *I. Fellowship Statistics.*

ON the 31st December, 1924, the number of Fellows was 3963. During the year 1925, 344 Fellows were elected and 10 reinstated, the gross total thus reaching 4317. The number of deaths recorded during the year was 40, as against 45 the previous year. The Council records a considerable falling off in the resignations received, the number being 88 as compared with 121 in 1924. The names of 105 Fellows have been removed from the List of Fellows owing to non-payment of annual subscriptions, and the election of one Fellow (in May 1924) has been declared void, the corresponding figures last year being 107 and 7, respectively. The number of Fellows at the 31st December, 1925, was, therefore, 4083, giving an increase of 120 over the preceding year. Among the Fellows who have died during the past year are Sir Edward Thorpe, who held the office of President from 1899-1901, of Treasurer from 1889-1899 and served on the Council for 40 years in all; Dr. Horace T. Brown, who was Treasurer from 1903-1904, Foreign Secretary from 1907-1913, and served on the Council for 20 years, and Professor F. R. Japp, who was Foreign Secretary from 1885-1891, and served on the Council for 16 years. The Council also mourns the loss of two distinguished Honorary Fellows, Professor Albin Haller (elected in 1908) and Professor Guglielmo Körner (elected 1898), the number of Honorary Fellows now being 24.

An obituary notice of Professor Körner, prepared by Professor J. B. Cohen, appeared in the Journal for December, and a notice of Professor Haller will be published in a forthcoming issue of the Journal. The Council takes this opportunity of recording its

appreciative thanks to those Fellows who kindly prepare for the Journal valuable notices of deceased Fellows.

The congratulations of the Council have been conveyed to Sir William A. Tilden (elected 1st June, 1865) and to Mr. William E. Bickerdike (elected 7th December, 1865), who have been Fellows for 60 years, and to the following, who, during the year, have attained their jubilee as Fellows :

	Elected.					
Alfred Southall	...	...	...	...	...	May 6th, 1875.
Pattinson B. Melmore	...	...	...	...	...	May 20th, 1875.
Sir Dugald Clerk	...	...	...	...	...	May 20th, 1875.
G. William Davey	...	...	...	...	...	Nov. 18th, 1875.
John F. M. H. Stone	...	...	...	...	...	Dec. 2nd, 1875.
Sir Ernest H. Cook	...	...	...	...	...	Dec. 2nd, 1875.
Alfred Smetham	...	...	...	...	...	Dec. 16th, 1875.
Bernard Dyer	...	...	...	...	...	Dec. 16th, 1875.
William H. Watson	...	...	...	...	...	Jan. 20th, 1876.
Martin F. Roberts	...	...	...	...	...	Jan. 20th, 1876.
H. Wilson Hake	...	...	...	...	...	Jan. 20th, 1876.
William Foulkes Lowe	...	...	...	...	...	Feb. 3rd, 1876.
Harold Bailly Dixon	...	...	...	...	...	Feb. 3rd, 1876.
William A. Smith	...	...	...	...	...	Feb. 3rd, 1876.
Paul G. W. Typke	...	...	...	...	...	Feb. 17th, 1876.
Francis S. Earp	...	...	...	...	...	Feb. 17th, 1876.
John M. H. Munro	...	...	...	...	...	Feb. 17th, 1876.

The congratulations of the Society were conveyed to Professor B. Brauner on the occasion of the celebration of his 70th birthday held in Prague in May.

## II. *Changes in Officers.*

The Council has received with deep regret the resignation of Dr. Arthur W. Crossley from the office of President, owing to reasons of ill-health. The Council, in placing on record its warm appreciation of his eminent services and untiring devotion to the affairs of the Society, desires to express its best hope that his recovery may be speedy and complete.

## III. *Publications.*

The Journal for 1925 contains 2986 pages, of which 2902 pages are occupied by 409 memoirs and 32 notes, the remaining 84 pages being devoted to Obituary Notices, one lecture, the Report on International Atomic Weights, the Report of the General Meeting, and the Presidential Address. The volume of the preceding year contained 363 memoirs and 31 notes, occupying 2605 pages. The number of papers published in the Journal for 1925 is a record, the previous largest number being 400 memoirs and 11 notes, occupying 3258 pages of the Journal for 1923.

During 1925, 479 papers were considered by the Publication Committee; of these, 37 were declined.

The average interval between the dates of receipt and of publication of papers was 13 weeks in 1925 and 17 weeks in 1924.

A large amount of work is done willingly and efficiently by Referees, and the Council desires to place on record its appreciation of their services. The Council also desires to express its thanks to Professor Wynne for again seeing the August number of the Journal through the press, thus enabling the Editor to take some holiday. It feels, however, that the arrangements for editing the Journal are far from satisfactory so long as the work remains in one pair of hands. Under present conditions the Editor, in the absence of voluntary assistance, would be debarred from a holiday, and, in the event of accident or illness happening to him, there is no one to take over the editorial work until his return to duty. This matter is receiving the attention of the Council.

#### IV. *Library.*

During 1925 there were 6994 attendances in the Library as compared with 6652 in 1924, 4746 of these being made by Fellows of the Society, and 2248 by members of contributing Societies, while the number of books borrowed was 4950 as against 4509 the previous year. The Library has been increased by the addition of 265 books, 609 volumes of periodicals, and 163 pamphlets, the corresponding figures last year being 265, 560, and 164, respectively. The Library now contains 30,011 volumes, consisting of 9066 books and 20,945 bound volumes of periodicals.

In 1925 £1799 2s. 3d. was expended on the Library, towards which £681 15s. was contributed by the kindred Societies. The Council desires again to express its appreciation of the substantial help received from the contributing Societies. The assistance thus given facilitates progress towards the establishment of a complete chemical library.

The urgent need for additional space for the Library has been mentioned in recent reports, and the necessity for a workroom for cataloguing and repairing books is hardly less urgent. For the moment the question of Chemistry House is in abeyance, so that relief in that direction is unlikely in the near future. It has been decided to provide further shelf space for books by lining the north and east walls of the Council Room with adjustable steel bookshelves and erecting a cantilever gallery. The consent of His Majesty's Office of Works having been obtained, the work will be put in hand without delay. It is estimated that the cost will be about £250, and that the shelf space thus provided may be

sufficient to meet the demands of the Library for three, or perhaps four, years. In this connexion it will be necessary to remove the portraits of the Past Presidents now in the Council Room. These will be contained in a portfolio accessible to Fellows, and the names of the Past-Presidents will be inscribed on oak panels which will be placed on the wall in the Meeting Room.

Arrangements have been made during the year by which readers can obtain photostatic copies of printed matter in the Library. Considerable use has been made of the facilities thus afforded.

#### *V. General.*

The society was represented by a number of Fellows at the meeting held at the Royal Institution on June 16th to celebrate the discovery of benzene by Faraday. On behalf of the President, who was unavoidably prevented from attending as official representative, Sir William Pope presented an Address of Congratulation. Professor C. S. Gibson, Mr. A. J. Greenaway, and Sir William Pope attended as delegates of the Society the Fifth Congress of Applied Chemistry held in Paris in September, and Professor H. E. Armstrong gave an oration in honour of Chevreul at the Celebrations held in the same city a month later; while Professor J. B. Cohen was the Society's representative at the Celebrations of the 11th centenary of the foundation of Pavia University held in Pavia in May. At the invitation of the General Council of Medical Education and Registration, the Council appointed the President and Foreign Secretary to represent the Society at the Conference held in February to discuss general questions relating to the proposed revision of the British Pharmacopœia. Professor C. S. Gibson, Sir William Pope, and Professor J. F. Thorpe were appointed to represent the Society on the Federal Council for 1926; while Professor J. W. McBain and Professor J. C. Philip were reappointed for a further term of two years on the Editorial Board of the "Journal of Physical Chemistry."

The Society has continued to be represented on the Bureau of Chemical Abstracts by Professors C. S. Gibson, G. T. Morgan, J. F. Thorpe, and W. P. Wynne. During the year the Bureau's proposals for the change of the format of the abstracts in pure chemistry were accepted by the Council, and accordingly from January, 1926, onwards, "British Chemical Abstracts" is appearing in two sections dealing respectively with papers in pure and applied chemistry, in double-column quarto format, and without overlap in respect of the papers abstracted. These arrangements make possible the preparation of a single annual index covering the abstracts in both sections, and this index will be supplied (without

additional charge) to all who receive the "A" section or the "B" section or both. Fellows of the Chemical Society, who are not members of the Society of Chemical Industry, but who desire to receive the "B" abstracts, can obtain them for £2 2s. per annum.

The Anniversary Dinner was held at the Hotel Victoria on March 26th, 1925, Dr. Arthur W. Crossley, President, in the chair. The company present numbered 240.

This year, for the first time in the history of the Society, it has been decided to hold the Annual General Meeting and the Dinner elsewhere than in London, and arrangements have been made for both to take place in Manchester—the meeting in the University and the Dinner at the Midland Hotel. It is hoped this innovation will commend itself to country members, and that the attendance will be such as to justify the Council in holding the Annual General Meeting at other provincial centres from time to time.

The Special Lecture this session was delivered on February 11th in the Chemistry Theatre of University College, London, by Professor J. Barcroft, who chose as his subject "Hæmoglobin." Instead of arranging for an additional Special Lecture, the Council decided to try the experiment of holding informal lectures given by Fellows of the Society, and two such lectures have been arranged. The first, by Professor R. Robinson, who lectured on "Recent Researches on the Structural Relationships of some Plant Products," was held in the rooms of the Society on November 26th at 6 o'clock, instead of the usual hour of 8 p.m.; the second lecture will be delivered by Professor W. E. S. Turner on April 29th at 6 p.m.

The large attendance at the lectures indicates that they are appreciated, and the Council desires to express its warm thanks to those who place their services at the disposal of the Society in this connexion.

The hope expressed in the last Report that the difficulty in awarding the Harrison Memorial Prize might be overcome by an agreement with the Committee which promoted the memorial, to vary the terms of the Trust Deed by the omission of the latter part of Clause 9, has not yet been realised.

The Council has made a grant of £100, thus completing the £300 promised, towards the cost of publishing the "Annual Tables of Constants," and has contributed £50 towards the cost of the Scientific Exhibit at the British Empire Exhibition, 1925. By means of the Russian Fund, which was created in September 1921 to grant relief to Russian Men of Science and their dependents, the Council has been able to afford assistance to Madame Mendeléev. A letter of thanks from Madame Mendeléev appeared in the



Proceedings for 1926 (p. 2). The Russian Fund, which reached a total of £400 4s. 10d., has been closed, the balance of £7 7s. 10d. having been transferred to Publications Fund Account.

## RUSSIAN FUND.

Statement of Income and Expenditure, 1921—1925.

<i>Income.</i>			<i>Expenditure.</i>		
To Donations	£	s. d.	By Donations :	£	s. d.
from Fellows	400	4 10	Prof. Mikkola . .	20	0 0
			„ Tschugaeff . .	1	0 0
			„ Makovetzky . .	171	4 0
			„ Kononov . .	58	0 0
			American Relief		
			Fund . . . .	28	13 11
			Imperial War Relief		
			Fund . . . .	45	16 0
			Madame Mendelév	45	15 0
					370 8 11
			Printing . . . .		9 11 6
			Scientific Books . . . .		1 6 3
			Carriage of Books and Clothing . .		9 18 1
			Bankers' charges . . . .		1 12 3
			Balance in hand . . . .		7 7 10
					<u>£400 4 10</u>
					<u>£400 4 10</u>

JOCELYN THORPE,  
*Treasurer.*

The List of Fellows, which, owing to the call for economy, was not published in 1924, was printed in August, 1925, and issued to those Fellows who made application.

In accordance with the decision of the Council, copies of the Presidential Address, entitled "Universities as Centres of Chemical Research," delivered by Professor W. P. Wynne on March 26th, were distributed amongst Members of Parliament, various Government Officials, and educational bodies.

The attention of the Council has been directed to the use by Fellows of the letters "F.C.S." in advertisements. The Council deprecates the use of the letters in this connexion, since they do not denote a qualification and such use is misleading to the public.

Applications for Research Grants aggregating £1644 have been received during the year, and Grants amounting to £758 10s., as recorded in the Proceedings (see pp. 93 and 148), have been allotted. Since the total sum for which application was made far exceeded that available for distribution, prior consideration has been given to applications made by Fellows.

VI. *Financial.*

The balance representing excess of income over expenditure for 1925 is £466 4s. 3d. The income of the Society has increased by £1208 6s. 8d. over that of 1924, in spite of the fact that the admission fees (£528 in 1924) have not been available, and that there has been a diminution in income from advertisements (£25 3s. 7d.), from invested funds (£37 4s. 11d.), and from miscellaneous receipts and sales (£138). The source of the new income is to be traced to the decisions of the Council, reached in 1923 and in 1924, to charge an increased price for the Journal, Abstracts, and Annual Reports to the public, and to charge Fellows for the Annual Reports; also, for the first time there has been a substantial income from the Publications Fund. The total obtained under these heads during the year has been £6112 8s. 8d., as against £4522 17s. 10d. for 1924 (during which year some of the effects of the changes were beginning to be felt), and £3799 17s. 6d. for the previous year, that is, before the changes came into operation.

The expenditure side of the account shows that the cost of the Journal has increased by £223 12s. 3d., despite the fact that there has been a saving of £125 16s. on the preparation of Authors' copies. The cause of this increase is the enlargement of the Journal by 288 pages due to the publication of 409 memoirs in place of the 363 published in 1924. The cost of the Abstracts has increased by £394 17s. 8d., due to the number of pages in 1925 being 468 higher than in 1924. There is, however, no overlapping in the payment of editorial salaries, and for this reason a saving of £113 9s. 9d. has been effected. Judging by these figures it is evident that there is still an upward tendency in the curve representing the world's annual output of published chemical research, and that the apex of the curve has still to be attained. At the same time there seems to be no immediate prospect of the cost of printing being materially decreased and, until the curve flattens, the Society will have to meet a constantly rising expenditure.

Among the other items on the expenditure side it will be noticed that the administration expenses have increased by £190 2s. 7d., due, mainly, to an increase in the item for miscellaneous printing and stationery of £125 0s. 6d. It will be seen, however, that the cost of printing the List of Fellows has been more than met by a saving of £133 1s. 4d. in the cost of the Annual Reports.

The total market value of the invested funds of the Society is £40,474 10s. 5d., an increase of £1,709 3s. 4d. over the figure for 1924 despite the depreciation of trustee stock to the extent of £852 on the General Purposes Account and the sale of £662 7s. of 3½% Conversion Stock, value £500, from the Research Fund Account.

The outlook for the future is fairly promising because, during the year 1926, the full interest on the Pedler bequest will become available; moreover it is to be expected that increased receipts will be obtained from outside sales of publications. On the other hand, the Society will be faced with an increased expenditure due to the scheme for the superannuation of the staff, and also to the cost of fitting the Council Chamber with bookcases in order to meet the requirements of the library. Next year's balance will depend on the cost of the Journal and Abstracts, and it is to be hoped that the scheme of co-operation which has led to the founding of the Bureau of Chemical Abstracts will enable a saving to be made by the elimination of the overlap between the "A" and the "B" series.

*Publications Fund.* In the last report of Council it was stated that, notwithstanding the generous response by Fellows who had contributed £1434 17s. 1d. to the Publications Fund, if the Fund were to be made really effective it would be necessary substantially to increase it. With this object in view it was decided to issue an appeal to Manufacturers, and as a result the Publications Fund now stands at £4067 17s. 4d. Of this, £2166 was received from Manufacturers and other firms connected directly and indirectly with the Chemical Industries of the country and £100 as a grant from the Birmingham University Research Fund. The income derived from the Publications Fund, together with Subscriptions received during the year under review, amounts to £622 13s. 10d. This sum, in which are included £350 from the Government Publications Grant of the Royal Society, and £80 the income from the residue of the estate of the late Sir Alexander Pedler, has helped to meet the expenses of publication. It is anticipated that between £4000 and £5000 bequeathed to the Society by Sir Alexander Pedler will be made over to the Society during 1926; the Publications Fund will then have a capital sum of close upon £9000.

*Special Publications Fund.* In 1918, a Committee of Chemists was formed to prepare and publish chemical bibliographies and works of reference in the English language, and funds were collected. The scheme was abandoned, but funds amounting to £1896 8s. 4d. collected by this Committee have been handed over to the Society on the understanding that they would be used "for the purpose of promoting chemical publication, but not for the purpose of defraying the cost of the Society's ordinary publications." The Council accepted the funds on the conditions stated, and a Special Publications Fund has been created, the sum of £1600 being invested in Conversion Loan.

*Memorial Lectures.* During the year Vol. I of the Memorial Lectures has been reproduced by a phototype process and is sold

to Fellows at 9s., post free, and to the Public at 10s. 6d. The publication of this volume is being financed by means of the Special Publications Fund.

*Staff Superannuation Scheme.* Another matter which has received the serious consideration of the Council has been the necessity for making some provision towards the Superannuation of the Staff. A contributory scheme of insurance based upon a 10 per cent. premium of the salaries received by the Staff, and payable at death, or on retirement, has been instituted, 5 per cent. being contributed by members of the staff and 5 per cent. by the Society. It is realised, however, that the sums thus accruing on the retirement of the beneficiaries will be inadequate, and accordingly a Pensions Fund has been created with a view to amplifying the amounts received from the insurance policies. The general funds of the Society will thus be relieved from any sudden call they may have to face, and Fellows have been invited to contribute to the Fund.

*Sales of Publications.* The price to the Public of the "A" Abstracts in Pure Chemistry for 1926 has been increased from £2 10s. to £3 10s., and the price of the Journal and Abstracts together has been increased from £5 to £5 10s. to the Public, and from £4 5s. to £4 15s. to Fellows who require extra copies. In order that the Abstracts in the new format may reach the Fellows in as good condition as possible it has been decided to issue them flat and in envelopes.

*Advertisements.* It is hoped that with the increased facilities which the "A" Abstracts in the new format afford for displaying announcements, the income of the Society derived from advertisements will show a considerable increase in the forthcoming year.

A vote of thanks to the Auditors (Profs. J. F. Spencer, A. J. Allmand, and J. S. S. Brame) for their services, was proposed by the Treasurer, seconded by Prof. F. L. PYMAN, and carried unanimously.

Prof. H. B. DIXON proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council, and Committees for their services during the year. This was seconded by Dr. ALFRED RÉE and adopted, acknowledgment being made by Sir WILLIAM POPE.

On the motion of Prof. R. ROBINSON, seconded by Dr. D. C. HENRY, Prof. A. J. Allmand, Prof. J. S. S. Brame, and Dr. G. W. Monier-Williams were elected Auditors for the coming year.

Prof. T. S. PATTERSON then moved the following resolution :

"In view of the fact that the publication in the Proceedings of the Chemical Society of a list of titles of papers which have been received but not published and which—either because the Publication Committee considers them unsuitable or because the author

may be unable to accept alterations suggested by the referees or by the Publication Committee, or for any other reason—may not be published, is very prejudicial to the subsequent publication of these papers elsewhere and, by disclosing the fact that such work is in progress, unfair to the author, besides involving the Society in unnecessary and unjustifiable expense at a time when all possible economy should be exercised, this meeting recommends that the practice of publishing such a list be discontinued.”

This was seconded by Prof. F. J. WILSON and, after discussion, was put to the meeting, and declared lost.

The following resolution :

“That this meeting, being of opinion that the position of the Chemical Society would be strengthened and the membership increased by the institution of local sections, recommends the Council to take such steps as would render practicable the institution of local sections where they might be desired ”

also proposed by Prof. T. S. PATTERSON and seconded by Prof. F. J. WILSON, was discussed; on its being put to the meeting it was declared lost.

THE PRESIDENT then delivered his address, entitled “The Co-operation of Science and Industry.”

A vote of thanks to the President for his services in the chair during the past year, and for his address, requesting him to allow the address to appear in the Journal, was proposed by Prof. W. P. WYNNE, seconded by Prof. W. H. PERKIN, and carried with acclamation. The PRESIDENT acknowledged the thanks and proceeded to read the report on the election to vacancies on the Council, announcing that Prof. H. Brereton Baker had been elected President. Prof. Baker then took the chair and continued the reading of the report :

*Vice-Presidents who have filled the office of President.*—H. E. Armstrong; Arthur W. Crossley; Percy F. Frankland; W. H. Perkin; Alexander Scott; W. P. Wynne.

*Vice-Presidents who have not filled the office of President.*—J. B. Cohen; A. J. Greenaway; James C. Philip; Sir Robert Robertson; R. Robinson; N. V. Sidgwick.

*Treasurer.*—Jocelyn F. Thorpe.

*Secretaries.*—T. Slater Price; C. S. Gibson.

*Foreign Secretary.*—F. G. Donnan.

*Ordinary Members of Council.*—H. Bassett; D. R. Boyd; O. L. Brady; H. V. A. Briscoe; A. E. Dunstan; F. A. Freeth; F. W. Gamble; R. Whytlaw Gray; J. Kenyon; B. Lambert; T. S. Moore; T. J. Nolan; K. J. P. Orton; R. H. Pickard; B. D. Porritt; F. L. Pyman; G. Stubbs; F. J. Wilson.

### INCOME AND EXPENDITURE ACCOUNT

	<i>Income.</i>	£ s. d.	£ s. d.
To Life Compositions ... .. .			128 0 0
" Annual Subscriptions :—			
Received in advance, on account of 1925 ... .. .		1083 0 0	
" during 1925 " " " "		8130 0 0	
" " " " 1924 ... .. .		446 8 0	
" " " " 1923 and previous years ... .. .		16 10 0	
		9675 18 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet ... .. .		500 0 0	
		9175 18 0	
Add Arrears at date : £901 10s. ; Estimated to realise as per Balance Sheet ... .. .		500 0 0	
			9675 18 0
" Investments, Dividends on :—			
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock ... .. .		24 11 11	
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock, 1914/54 ... .. .		35 18 8	
£1400 India 2½ per cent. Stock ... .. .		35 0 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock ... .. .		48 0 0	
£2718 London, Midland and Scottish Railway 4 per cent. Preference Stock ... .. .		84 15 7	
£1200 Leeds Corporation 3 per cent. Stock ... .. .		28 7 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53 ... .. .		45 0 0	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock ... .. .		28 2 6	
£700 Canada 5½ per cent. Stock, 1930/50 ... .. .		19 5 10	
£2100 5 per cent. War Stock, 1929/47 ... .. .		105 0 0	
£1100 5 per cent. War Bonds, 1929/47 ... .. .		44 0 0	
£600 Funding Loan, 4 per cent., 1960/90 ... .. .		24 0 0	
£11878 3¼ per cent. Conversion Stock ... .. .		874 0 0	
" Income Tax Recovered ... .. .		137 5 8	
" Interest on Deposit ... .. .		51 4 11	
			1084 11 8
" Publication Sales :—			
Journals and Proceedings ... .. .		2668 11 0	
Abstracts ... .. .		2067 0 7	
Collective Index, Vols. I-V ... .. .		64 4 6	
Annual Reports on Progress of Chemistry ... .. .		759 3 8	
Berichte ... .. .		22 0 0	
		5575 19 4	
Less Publishers' Commission ... .. .		513 19 9	
			5061 19 7
" Proceeds of Advertisements in Journal and Abstracts ... .. .		596 17 0	
Less Commission ... .. .		57 11 8	
			539 5 4
" Miscellaneous Receipts... .. .			25 10 9
" Donations to Library :—			
Association of British Chemical Manufacturers ... .. .		250 0 0	
Biochemical Society ... .. .		10 10 0	
Faraday Society ... .. .		5 5 0	
Institute of Brewing ... .. .		45 0 0	
Institute of Chemistry ... .. .		250 0 0	
Society of Chemical Industry ... .. .		100 0 0	
Society of Dyers and Colourists ... .. .		10 10 0	
Society of Public Analysts ... .. .		10 10 0	
		681 15 0	
" Pedler Bequest, Income from Residue of Estate of Sir Alexander Pedler		80 0 0	
" Subscriptions from other Societies ... .. .			28 17 6
" Transfer from Publication Fund, viz. :—			
Government Publications Grant (through the Royal Society) ... .. .		350 0 0	
Dividends and Interest on Deposit ... .. .		184 3 4	
Subscriptions ... .. .		88 10 6	
			622 13 10
			£17,923 11 1

FOR THE YEAR ENDED 31ST DECEMBER, 1925.

*Expenditure.*

	£	s.	d.	£	s.	d.
By Expenses on account of Journal :—						
Editorial Salaries ... ..	880	0	0			
Editorial Postages ... ..	69	10	7			
Printing of Journal ... ..	3423	15	1			
Banding ... ..	69	7	5			
Printing of Advertisements ... ..	128	17	8			
Addressograph Labels ... ..	5	14	1			
Distribution of Journal ... ..	474	9	5			
Authors' Copies ... ..	312	8	9			
Insurance of Stock ... ..	5	5	0			
Warehousing of Stock ... ..	5	10	2			
				5303	18	2
„ Expenses on account of Abstracts :—						
Editorial Salaries ... ..	1085	0	0			
Editorial Postages ... ..	34	10	0			
Abstractors' Fees ... ..	1287	11	11			
Printing of Abstracts ... ..	3028	8	10			
Banding ... ..	69	7	4			
Addressograph Labels ... ..	5	14	2			
Distribution of Abstracts ... ..	474	9	5			
Insurance of Stock ... ..	5	5	0			
Warehousing of Stock ... ..	5	10	2			
Miscellaneous ... ..	61	17	2			
				6055	14	0
Lecture Expenses ... ..						27 11 6
Advance Proofs and Reports of Meetings ... ..						84 17 3
Annual Reports on the Progress of Chemistry ... ..						528 15 1
Purchase of Back Numbers of Journal ... ..						13 18 10
List of Fellows—Printing, etc. ... ..						126 2 0
Library Expenses :—						
Salaries ... ..	1185	10	0			
Books and Periodicals ... ..	488	7	6			
Binding ... ..	130	4	9			
				1799	2	3
Donations :—						
Annual Tables of Constants ... ..	100	0	0			
British Empire Exhibition ... ..	50	0	0			
				150	0	0
Administration Expenses :—						
Salaries of Staff ... ..	1427	12	9			
Wages (Commissionaire, Housekeeper, and Charwomen) ... ..	414	6	0			
Pensions ... ..	16	5	0			
Coal and Lighting ... ..	83	12	1			
House Expenses and Repairs ... ..	109	16	3			
Telephone ... ..	22	0	2			
Tea Expenses ... ..	43	0	3			
Insurances ... ..	25	0	4			
Accountants' Charges ... ..	31	10	0			
Commission on Recovery of Income Tax ... ..	6	17	3			
Miscellaneous Printing and Stationery ... ..	472	3	7			
Postages ... ..	201	13	1			
Legal Charges ... ..	10	10	0			
Carriage on Journals to Germany ... ..	16	7	11			
New Press and Renovating Seal ... ..	16	0	0			
Addresses ... ..	14	14	0			
Miscellaneous Expenses ... ..	80	8	3			
				2991	16	11
Transfer to Publications Fund (Life Composition Fees) ... ..				123	0	0
Publications Fund—Income from Pedler Bequest ... ..				80	0	0
Collective Index Vol. VI ... ..				112	11	5
Excess of Income over Expenditure carried to Balance Sheet ... ..				466	4	3

£17,923 11 8

RESEARCH AND OTHER FUNDS INCOME AND EXPENDITURE ACCOUNTS FOR THE YEAR ENDED 31ST DECEMBER, 1925.

**RESEARCH FUND.**

	Income.	£	s.	d.	£	s.	d.	Expenditure.	£	s.	d.
To Dividends on :											
£1000 London and North Eastern Railway 4 per cent. 2nd								By Grants	...	...	...
Guaranteed Stock	...	...	...	...	31	5	0	" Commission on Recovery of Income Tax	...	...	...
£1034 Great Western Railway 3½ per cent. Debenture Stock	...	...	...	...	20	3	11	" Advertisements	...	...	...
£1143 16s. New South Wales 8 per cent. Debenture Stock	...	...	...	...	34	5	8				
£1122 Metropolitan Water Board 3 per cent. "B" Stock	...	...	...	...	83	13	2				
£353 London, Midland and Scottish Railway 4 per cent.	...	...	...	...	26	13	1				
Debenture Stock	...	...	...	...	19	0	10				
£806 Victoria 8 per cent. Stock, 1929/40	...	...	...	...	234	18	6				
£4498 11s. 0d. 5 per cent. War Loan, 1929/47	...	...	...	...	192	7	0				
£5164 13s. 9d. 3½ per cent. Conversion Stock	...	...	...	...	582	7	2				
Income Tax Recovered	...	...	...	...	50	17	4				
Repayment of Grants	...	...	...	...	111	5	8				
Interest on Deposit	...	...	...	...	4	17	0				
Balance, being Excess of Expenditure over Income,	...	...	...	...	17	11	8				
carried to Balance Sheet	...	...	...	...							
					£766	13	10				

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

[illegible]



PUBLICATIONS FUND.

<i>Income.</i>		<i>Expenditure.</i>	
£	s. d.	£	s. d.
To Transfer from General Account, being Life Composition			
Fees for year	123 0 0	By Transfer to General Account—Income applicable to 1925	
" Subscriptions	101 0 0	Publications, viz.:	
" Donations	2395 14 4	Government Publications Grant (through the Royal	
" Interest on Deposit	20 19 2	Society)	350 0 0
" Government Publications Grant (through the Royal		Dividends and Interest on Deposit	181 3 4
Society)	550 0 0	Subscriptions	83 10 0
" Dividend on £4623 4s. 10d. Conversion Stock, 8½ per cent.	88 4 2	" Subscriptions in advance	623 13 10
" Transfer from General Purposes. Income from Pedler	80 0 0	" Balance, being excess of Income over Expenditure,	12 10 0
" Bequest		carried to Balance Sheet	2518 14 4
	<u>£3153 18 2</u>		<u>£3153 18 2</u>

SPECIAL PUBLICATIONS FUND.

To Sales of Publications:—		By Cost of Reproduction:—	
Memorial Lectures, Vol. I	52 10 0	Memorial Lectures, Vol. I.	225 3 0
" Balance, being Excess of Expenditure over Income carried to	172 13 0		
Balance Sheet	<u>£225 3 0</u>		<u>£225 3 0</u>

STAFF PENSIONS FUND.

To Subscriptions	15 15 0	By Excess of Income over Expenditure carried to Balance Sheet	15 15 0
	<u>15 15 0</u>		<u>15 15 0</u>

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31ST DECEMBER, 1925.

GENERAL PURPOSES.		RESEARCH FUND.	
£	s. d.	£	s. d.
<b>Liabilities</b> To Subscriptions received in advance ... " Sundry Creditors (Printing and other Expenses) ... " Excess of Assets over Liabilities as per last Balance Sheet ... Add Excess of Income over Expenditure for Year ...		<b>Assets</b> By Investments (value when acquired):— £757 London, Midland and Scottish Railway 4 per cent. Debenture Stock ... £1400 India 3½ per cent. Stock ... £2400 Bristol Corporation 2½ per cent. Debenture Stock, Bristol Dock Account ... £2718 London, Midland and Scottish Railway 4 per cent. Preference Stock ... £1200 Leeds Corporation 5 per cent. Stock ... £1500 Transvaal 5 per cent. Guaranteed Stock, 1922-53 ... £1200 London and North Eastern Railway 5 per cent. Debenture Stock ... £700 Canada 3½ per cent. Stock, 1939/50 ... £2100 5 per cent. War Stock 1939/47 ... £1100 5 per cent. National War Bonds, 1939/47 ... £800 4 per cent. Funding Loan, 1960/90 ... £11,875 3½ per cent. Conversion Stock ... (Market Value £21,732 3s. 2d.) Sundry Debtors ... " Subscriptions in Arrear £901 10s. Estimated to realise ... " Insurance paid in advance ... " Cash in Hand ... " Cash at Bank ...	
25,660	6 5	20,206	3 3
466	4 3	25,068	18 10
26,126	10 8	500	0 0
		52	9 3
		647	18 4
		£30,092	3 2
14,462 4 2 17 11 8 14,444 12 6		1010 0 0 1049 15 11 1000 0 0 1002 16 9 1000 18 9 426 6 2 430 10 0 5898 14 10 18,044 17 3 99 15 8 400 0 0 £14,444 12 6	
To Excess of Assets over Liabilities as per last Balance Sheet ... Less Excess of Expenditure over Income for Year ...		By Investments (value when acquired):— £1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock ... £1034 Great Western Railway 2½ per cent. Debenture Stock, 1862-82. New South Wales 5 per cent. Stock ... 1895 £1123 Metropolitan Water Board 5 per cent. "B" Stock ... £863 London, Midland and Scottish Railway 4 per cent. Debenture Stock ... £808 Victoria 5 per cent. Stock, 1929/49 ... £4498 11½ 0½ 5 per cent. War Stock, 1939/47 ... £5164 18s. 3d. per cent. Conversion Stock ... (Market Value £12,574 18s. 10d.) " Cash at Bank ... " Current Account ... " Deposit Account ...	

## THE EDWARD FRANK HARRISON MEMORIAL TRUST

To Excess of Assets over Liabilities as per last Balance Sheet ... ..  
 Add Excess of Income over Expenditure for Year ... ..

£	s.	d.	£	s.	d.
1251	6	8	500	0	0
54	8	8	500	0	0
			50	1	5
			1050	1	5
			55	13	6
			200	0	0
			255	13	6
			£1805	14	11

By Investments (value when acquired):—  
 £500 National War Bonds 5 per cent. 1928 ... ..  
 £500 National War Bonds 5 per cent. 1929 ... ..  
 £61 15s. 8d. 34 per cent. Conversion Stock ... ..  
 (Market Value £1098 9s. 8d.)  
 Cash at Bank ... ..  
 Do. ... ..  
 Current Account ... ..  
 Deposit Account ... ..

## PUBLICATIONS FUND

12	10	0
1536	13	0
2518	14	4
4055	7	4
£1087	17	4

By Investment £4023 4s. 9d. 34 per cent. Conversion Stock ... ..  
 " Life Composition Fee (Market Value £2478 19s. 8d.) ... ..  
 " Cash at Bank on Current Account ... ..

3500	0	0
18	0	0
549	17	4
£4067	17	4

## SPECIAL PUBLICATIONS FUND

1896	8	4
172	13	0
1723	15	4
£1723	15	4

By Investments:—  
 £2115 8s. 10d. 34 per cent. Conversion Stock (Market Value £1692 4s. 11d.) ... ..  
 " Sundry Debtors for Sales:—  
 Memorial Lectures Vol. I ... ..  
 " Cash at Bank ... ..

1600	0	0
45	15	0
78	0	4
£1723	15	4

## STAFF PENSIONS FUND

£15	15	0
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By Cash at Bank ... ..

£15	15	0
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KK

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments.

W. B. KEEN,  
 Chartered Accountant.

23, QUEEN VICTORIA STREET, E.C. 4  
 February 10th, 1926.

Approved { J. F. SPENCER,  
 A. J. ALLENBY,  
 J. S. S. BRANE.

## PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING held in Manchester on March 25th, 1926.

By ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S.

THIS is the first occasion on which the Chemical Society has departed from a custom, which has persisted since its foundation in 1841, namely, that of holding all its official meetings at its premises in London. The opinion has often been expressed that our provincial members do not have a sufficient say in the management of the Society's affairs, and certain alterations of Bye-Laws have recently been made, which materially affect this state of affairs. When the suggestion was made to the Council that every alternate Annual Meeting should be held in the Provinces, it was unanimously accepted and it is by virtue of that decision of the Council that we meet to-day in Manchester.

It seems particularly appropriate that our meeting should be in this Institution and in this lecture theatre; for through the Professors who have taught here and who have also been Presidents of the Chemical Society there are very close ties with us, and I am confident that I may record the most grateful thanks of the Society to the University of Manchester for granting permission for us to assemble here to-day.

The first professor of chemistry in the Owens College was Edward Frankland (1851—1857), who was President of our Society from 1871—1873. For the twenty-nine succeeding years, 1857—1886, he was followed by Henry Enfield Roscoe, who was President of the Chemical Society in 1880—1882. It was my privilege to be one of the later students of Sir Henry Roscoe, and I have often heard him lecture in this room. He was truly a remarkable teacher and one who had a very unusual hold and influence on his students. He was not a polished lecturer from the point of view of delivery, nor because he gave deep-seated discourses into abstruse chemical problems, but he was a lecturer who had the faculty of interesting his students in a marked degree, in consequence of which they became anxious to learn for themselves. That, to my mind, is the essence of real teaching.

Roscoe was followed in 1886 by Harold Baily Dixon, who occupied the Chair for thirty-seven years, namely, until 1923, and who was President of our Society during the period 1909—1911. My main student years were spent under his direction, but since he is here with us to-day, I will only say of him that he is as young as ever,

still hale, hearty, and active. Long may he remain so! There is, however, one very special reason why we may to-day offer him our warmest congratulations, inasmuch as he was elected a Fellow of our Society in 1876 and has therefore attained his Jubilee of Fellowship.

Two other past Presidents of our Society have also been Professors in this University: Professor W. H. Perkin, who was Professor of Organic Chemistry from 1892—1912 and our President for the period 1913—1915, and Sir William Pope, who was Professor of Applied Chemistry from 1905—1908 and our President from 1917—1919. To them also we would express our sincere wishes for long-continued health and activity.

*The Co-operation of Science and Industry.*

It is a simple economic fact that since this country does not produce a sufficiency of foodstuffs to feed its population, it must manufacture goods and sell these in foreign markets at a profit, in order to purchase the food which is necessary to sustain life. The more the population grows, the more of our manufactured goods must be sold abroad, if our existence is to continue. It follows from this fact that the maintenance of our industries is a national necessity, and they must not only be maintained on the same standard as in the past, but we must always be attempting to reach a higher efficiency, in order to cope with foreign competition. There was a time when Great Britain, as the pioneer of industrial development, could afford to select her own pace and her own methods, for she alone was in the field. The results obtained, largely without the aid of science, were indeed astonishing, but they came as a result of the breaking of new ground. Virgin soil may give wonderful crops for a few years, but to take from it continually and give nothing to it spells, as everyone realises, ruination, and in order to maintain the harvest it is necessary to nurture the soil or to manure it.

British industry worked on virgin soil in the past, and has worked it well-nigh to starvation point, owing to the lack of appreciation of the importance of science generally from the point of view of our national welfare. Numberless examples of the importance of science to industry and to the general welfare of mankind have been and are being constantly brought to our notice, and the years 1914—1918 gave signs that the nation had at last realised that science and scientific method were our only hope. Yet the lesson then apparently learnt seems to have been forgotten, because as a nation we still fail to realise that all real industrial progress is the result of the application of scientific facts and data and that those

who fail to utilise science to the full must inevitably fall behind in the race of nations which is now in progress.

Instead of being, as in the past, almost the only industrial nation, we now realise that other peoples have become industrialists, to whom we have given all our past experience. But they have forged ahead owing to their full appreciation of the possibilities of science in its application to industrial problems; from being the teachers in the past, we have now become pupils, and not very apt or willing pupils at that. We do not seem able to forget our unprecedented and unopposed success in the past; we think the same methods should still lead to success now and in the future, and we waste much precious time in wondering why our industries are not as prosperous as they used to be.

We can scarcely look for more new raw material within the country other than brains, in which respect we have good reason to think that our raw materials are at least equal in quality to those of any other country. Our brains must be used to resuscitate our industrial soil, which must be nurtured or manured, and new scientific facts and data are the nourishment which must be given if industry is to continue to be a profitable undertaking; if we are to be, I will not say as successful as we were in the past, but if we are to hold a place amongst the foremost nations of the world, or if our existence as a nation is to continue.

An anonymous author writes\* as follows in the *Round Table* under the heading "British Industry and the Future":

"It is not only in the actual processes of manufacture that science can be used, but in the whole conduct of business, from the purchase of raw materials and the distribution of machinery, to the training and selection of labour, transport and sales. All these problems are more or less solved by a business that pays its way, but in too many cases rule of thumb and antiquated methods make the yield much poorer than it might be. For the higher branches of management there is little or no systematic training attempted. . . . In an age of super competition nothing but the best-equipped brains will be able to stand the pace. . . . Modern industry is as complex and difficult a profession as any. Its leaders need as thorough and prolonged an intellectual training as the doctor or the lawyer."

If a country can manufacture goods of superior quality, of constant novelty or of exceptionally high performance, at reason-

\* Several quotations in this paper are from an article entitled "British Industry and the Future," to be found in the September 1925 number of the *Round Table Review*; also from a pamphlet "What Price Progress", published by the "Chemical Foundation," New York, 1925.

able prices and keep on doing so, other countries are compelled to buy from it. Science is the modern key to such a situation and new discoveries in science are essential to maintain the industrial position of this country; in fact, science is the sentinel that must be posted at the door of every business house with the main object of preventing loss from want of knowledge. If we look round, surely nothing can bring greater hope to us than the realisation of the many comforts we enjoy as the result of research—electric light, the telephone, the telegraph, wireless, the internal combustion engine, to mention only a few of the more obvious.

But on one point let there be no doubt; although science should bring great hope to all for the future, it gives no hope whatever for less strenuous efforts, but rather the reverse. Science of all taskmasters is the hardest, the most uncompromising, the most severe, punishing relentlessly any slack or slovenly work done in her name and exacting to the uttermost limit faithful and untiring devotion, if she is to reveal her secrets.

It is always interesting to know the opinions of successful men on such matters, and Mr. Filene, an American business magnate, writes in his book, "The Way Out," as follows :

"This period will ultimately witness a ruthless weeding out of 'the businesses that do not go beyond mere price cutting and 'wage slashing. The survivors will be the businesses in which 'waste has been conquered and scientific method introduced."

Again the American wood alcohol industry has recently suffered a severe check as the result of a new scientific discovery, and in commenting on the fact a celebrated American professor of chemistry says :

"American manufacturers have failed, on the whole, to understand the need for research to keep their industries at the front. 'The backwardness of the manufacturer in this respect only reflects 'that of the general public in this country. The principal trouble 'here, in comparison with Germany, France, and England, is that 'we do not appreciate to the same extent the significance of science 'to the present day civilisation. . . . The whole thing will have its 'value if it is appreciated by American manufacturers and the 'public, as an object lesson of our backward-looking attitude 'towards research."

This writer is evidently of opinion that the general appreciation of the importance of research is greater in this country than in America. Although I have no personal knowledge of America, I do not think this can be possible, nor does the writer in the *Round Table* who, in comparing the trade possibilities of this country and America, points to many of the immense initial trade advantages

possessed by America, and then adds : " If, in addition, they obtain a lead in the application of science to industry it is difficult to see how we can hope to compete with them."

It is not only research that is needed in this country, but research on well-ordered and organised lines. If the suggestion made at the first meeting of the British Association had been carried into effect it is probable that the general appreciation of the importance of science in this country would now have been widespread : but as it is, research has been allowed to be carried out by the individual on his own lines and in accordance with his own fancies, without in any way attempting to produce organised effort for the general welfare of the nation ; and the pure research worker has been left to himself to become " a member of a priesthood which prides itself on its detachment from worldly things, a priesthood which refuses admission to any who bear the taint of hope of material gain."

Yet despite this splendid isolation of the pure research worker, what a glorious record of important discoveries is his and how much his country might have benefited if some few of them had been put to industrial use here, instead of becoming milestones in the development of foreign industrial capacity.

It was not until 1914 that any real attempt was made to organise the scientific workers of this country, with what results everyone knows and we have to thank some unknown persons whose ideas led, in July, 1915, to the establishment of an Advisory Council to make recommendations and proposals for :

I. Instituting specific researches.

II. Establishing or developing special institutions or departments of existing institutions for the scientific study of problems affecting particular industries and trades.

III. The establishment and award of Research Studentships and Fellowships.

From this suggestion has developed the Government Department of Scientific and Industrial Research, which in the short time it has existed has done more for the organisation of scientific effort than has ever before been done in this country.

Professor Wynne in his Presidential Address last year spoke in no uncertain terms of the benefit which had accrued to research students as the result of research grants made by the Department, and I need not refer further to item III above. Those who are interested in the other activities of the Department will do well to study somewhat carefully its annual report for the year 1924—1925. Under item I above are included such important problems



as researches connected with fuel, building materials, illumination, adhesives, forest products, foods and cold storage, and many others which have been initiated as a result of co-ordination of research in Government Departments by a series of co-ordinating Research Boards. And under item II come the National Physical Laboratory, the newly-established Chemical Laboratory, the Geological Survey and Museum of Practical Geology, the British Museum Laboratory and Industrial Research Associations.

Many of the difficulties of applying science to an industry as a whole were evidently fully appreciated by the Committee of the Privy Council, and under the title "Impediments to Industrial Research" the following words appear in the Report of the Committee for 1915-1916\* :

"Our experience up to the present leads us indeed to think that the small scale on which most British industrial firms have been planned is one of the principal impediments in the way of the organisation of research, with a view to the conduct of those long and complicated investigations which are necessary for the solution of the fundamental problems lying at the basis of our staple industries. What, for instance, is the exact nature and constitution of the cotton fibre, of rubber or of the resins? How does the structure of an alloy depend on its chemical composition and on its mechanical and heat treatment? . . . These are questions which none but the greatest of individual firms or a big combination of firms could venture to attack."

Yet the initial difficulties seem to have been overcome with great skill and Research Associations have been formed by specific industries, on the principle that the Department would provide money in definite proportion to the amount raised by the industry and would continue these grants for five years. In the case of the cotton industry, the subscriptions from the trade are regulated by the number of spindles or looms in a mill or by the declared capital of the company, and are on a unit principle. Since nearly 90 per cent. of all the firms in the industry are members of the Research Association, and also owing largely to generous help which has been afforded by the Cotton Trade War Memorial Fund Committee, the annual income of this Association is for the next four years approximately £54,000. It has therefore been possible to establish laboratories wherein "the fundamental problems lying at the basis" of the industry can be attacked, for which purpose organised and co-operative research is absolutely necessary. It is true that there are many purely botanical, chemical, or physical

\* Report of the Committee of the Privy Council for Scientific and Industrial Research for the year 1915-16, page 25.

problems to be solved, but fundamental research directed towards the general advancement of this industry more often than not means the close co-operative efforts of botanist, chemist, and physicist, and where results are forthcoming, further co-operation with technical men and practical works experience become essential.

Undoubtedly, organised research has been carried on in the past by some firms or industries—the results achieved allow us to make this deduction; but the information gained has naturally remained the property of the firms concerned and does not touch the national programme of scientific work. The aim of the Department's scheme is to advance the industry as a whole.

The grants made by the Department were originally for five years, in which time it was hoped that the Associations would have done so much for their trades that further Government help would not be necessary. But the First Report of the Committee of the Privy Council (page 30) contains these words: "The shortest period in which any considerable results can be expected is five years, while results so considerable as to affect the whole industry cannot be looked for in less than ten years' consecutive work." It has now been proved that five years is too short a time in which firmly to establish such an enterprise, which necessitates the selection of a scientific staff, the building of laboratories, and the collection of a library, together with other research facilities. The British Cotton Industry Research Association was founded in 1920, its laboratories were opened in March, 1922, and it is only now, six years after its creation, that the Association is really getting into intimate contact with the trade, which is recognising that science is capable of rendering assistance. It may appear to some that progress from the point of view of the trade has been slower than it should have been and it is just possible that more work of immediate use to the trade might have resulted, if those responsible for the foundation of the Association had not decided that the large fundamental problems lying at the basis of the industry were to be the main objects of inquiry. But the founders made a wise decision, for although initial advances may have been slow, future progress will be greatly accelerated by the better understanding of these fundamental problems.

The idea of these Research Associations and the plan on which they have been brought into being seem to me to be the only possibility for the general introduction of science and scientific method into some of our large industries, and the work of the Department in this direction is destined to prove of immense value to the trade of this country, indeed it would not appear too much to say that the whole concept is one of the utmost national importance. The

movement must lead ultimately to greater trade efficiency, to the expansion of trade, and to greater employment both of scientific and industrial workers.

Further, the movement has led to the increase of the number of research workers in laboratories connected with individual firms, and will lead to the larger employment of scientists in works, to establish scientific control, and to form the intelligence departments which will search into the results obtained and endeavour to apply them to industrial progress.

But the Department's scheme has none the less been severely criticised, largely by those who are always willing to pour forth destructive criticism, without attempting to supply anything in the nature of a constructive policy.

Sympathy has often been expressed for me in my supposed efforts to divest my surroundings of Departmental red tape, which, as my well-wishers put it, must stifle any freedom of action relative to research. I can only say that I have not encountered any of this flaming cord. Naturally an Association receiving money from public funds must be required to conform to certain rules and regulations, but these have not been in any way irksome, nor have they in the least interfered with research progress. On the other hand, I am glad to have this opportunity of acknowledging the great help which the Association has received from the Department on all and every occasion on which such help has been sought. One of these aids, which is becoming of increasing importance, is the Department's Information Bureau, which not only serves as a clearing house for research information relative to this country, but is taking on a much wider scope.

It has been frequently urged that it is undesirable, not to say wrong, to devote public money to industrial research, which should be supported entirely by the trade concerned. There is, I think, a very good answer to this criticism. Truly successful research is rarely without benefit to mankind at large and one need not do more to emphasise this point than refer to the life work of such a man as Pasteur. As regards industrial research, it may safely be said that the fruits of such research are always for the public benefit. It has been estimated, for example, that the research work of the General Electric Company of America is saving the American nation at least a billion dollars a year in the matter of electric light.

Those industrialists who found research laboratories with the avowed intention of investigating the fundamental problems of their industries, of ascertaining all there is to be known about the materials which they use, do so perhaps mainly in the hope that

their businesses will thereby be expanded, as the result of the introduction of new or the improvement of old materials and processes. They further realise that this must lead to greater employment, both industrial and scientific, for scientifically controlled production means methodically certain production, with less expense of mental effort and therefore more of the latter for devotion to other work. But they take a chance, for no one can assure them that results of value will be obtained in any stated period. When, however, results are forthcoming, the public, which has staked nothing, gets the benefit every time, whether it be in the way of electric light, artificial silk garments, or more skilful medical treatment. Why, then, should not the public contribute to the cost of research from the results of which they benefit so largely?

But no matter how much criticism is levelled at the Department of Scientific and Industrial Research, it still remains a fact that its activities have led to an organised effort to bring science and industry together, an effort which has already been crowned with distinct success and will lead to a great future, if all those interested will look at the movement in the true national spirit and do what they can to support and further it. For in reality it is a distinct step towards the organisation of the immense research power of this country.

If, however, the results of research are to be effectively applied, it is absolutely necessary that industry should meet science at least half-way. It is useless for the industrialist to complain that he does not understand scientific papers and that they must be put into everyday language, so that he *can* understand them. It is not to be expected that every industrialist can be a trained scientist, but he can at least guard himself by employing trained scientists in his business, thus establishing the position of the man of scientific training in industrial management. The position could not be more clearly stated than in the following words of the Prime Minister, when speaking in the House of Commons in the summer of 1925 :

"No one will assert that British industry can be saved by science alone, but it is none the less true that until scientific methods and scientific men can take their place in industry and an equal place with the administrator and the financier, British trade will never be strong enough or resilient enough to meet the shocks that it is bound to meet as the years go by, or to meet the sudden and unexpected changes which will always arise in international trade."

Reference has just been made to the immense research power possessed by this country. Are there not other ways in which this power can be put to the nation's benefit? Cannot we so organise

ourselves that at all events some portion of this vast research force is utilised in the solution of some of the problems which are vital for our welfare? In foreign countries much of the research energy of the Universities and higher Technical Institutions is directed by the Professor, himself in the closest contact with the heads of some great industry, towards the solving of important technical problems. Immediate solution is not looked for, but gradually a mass of new information is forthcoming, which in very many cases has led to results of the greatest importance, in regard to the elimination of waste, the utilisation of what have been regarded up to the time as waste products, and the discovery of new materials of commercial value. Frequently this means that a young scientist is sent into a works to watch his laboratory experiments gradually translated into manufacturing possibilities and hence the Professor and also the works authorities have opportunity of judging in which direction his future capacity lies, whether solely for pure research or for the application of science to works problems, etc.

Could not funds be found from somewhere to provide for the training in research method of those who are willing to undertake work on one of the many urgent national problems?

Cannot facilities be provided for sending trained men of science at an early point in their industrial career, to study the industrial methods of other countries?

Neither science alone nor industry alone can set any such ideas in motion, it is only by the honest and hearty co-operation of both sides that any success will be gained.

Is there any amongst us who can truthfully say, These are matters which do not interest or affect me and towards the solution of which I can add nothing of value? Surely, as a result of the simple fact with which I opened my remarks, we are all, without exception and no matter what our every-day work is, ultimately dependent for our existence on the success of our great industries, and although there may be some slight indication of trade improvement, the present situation is sufficiently serious to warrant every thinking man making it the principal national thought for the time being.

Someone has said that the Britisher is a confirmed individualist, from which fact his failures and his successes have arisen; but is it not time that we brought ourselves to realise that there is much unselfish and co-operative national work to be done? The never-ending search for new knowledge is the exacting price which must be paid for survival under modern industrial conditions.

There is another important aspect of the situation which I should like to consider for a few moments: as a teacher, or at all events one who, if not active at the present, has spent a large portion of

his life in the teaching of chemistry, I would ask if we are satisfied that we are doing all in our power to train up a body of young chemists, who will be able to fill the openings which industrial life offers and will in future offer always in increasing numbers, provided we continue to progress. I have given much consideration to this question, especially during the past six years, and I am bound to say that I do not think a wholly positive answer can be returned to the question. One often hears it urged as a serious fault of British manufacturers trading in foreign markets that they supply goods which they "think should be required" by the said markets without troubling to ascertain whether the purchasers have any tastes, desires, or special requirements of their own or whether their natural surroundings render desirable modification of goods made for this country, whereas our competitors do make the necessary inquiries and are constantly reaping the benefit. I rather think the same accusation might legitimately be brought against the teachers of chemistry in this country, who might be considered to be providing chemists who have had the training which the teachers "think should be required" by industry, without troubling to inquire whether industry has any special needs of its own, whether industrial surroundings demand special consideration, or whether one industry differs in its requirements from another. It is granted that such inquiries would demand more than a bowing acquaintance with any special industry. Is it not, however, the duty of the teacher to make such inquiries as equally, in my opinion, it is the duty of the industrialist to make known his requirements to the teaching profession?

It needs but little consideration of the question to reveal the fact that industry requires chemists with broadly differing lines of training, according to the special branch they are going to take up. To my mind, our present training is much too stereotyped, leading to the production of one type of man only. The system produces many extraordinarily good men of this type, but it leaves out of consideration the fact that there are many differing types of men who are not all capable of showing their best qualities as a result of one set method of training.

Take, for example, the industry with which I am connected, namely, the cotton industry; here the chemist has to deal with a biological entity, and if he has not had a training in some biological subject and cannot think from the biological standpoint, much of his time and of his employers' time will be wasted, for it is hopeless to look upon the cotton hair as a definite "substance" from the chemist's point of view.

Among the various types of chemists required by industry is

the research worker pure and simple, who will be free to devote his abilities solely to the advancement of knowledge and who need not of necessity have any business qualifications or adaptability for applying his knowledge to industrial problems. He may be the true specialist in some branch of his science.

A second type of chemist, quite as rare as the true research worker, quite as important in industry, and yet possessing an entirely different outlook of mind, is the man who can apply new scientific data to industrial development and can convert laboratory experiments into industrial operations. Then there is the process chemist, whose duty is not the furtherance of abstract knowledge, but the careful scientific control of works processes. He again is a most important type, for there are few industries in which better technical results could not be obtained by more careful scientific control. One of the main requirements from such a man is his capacity to do, or to supervise, accurate analytical work, requiring frequently a high order of attainment as an analyst, a qualification not always demanded by our present examination system. As a fourth type may be mentioned the chemical engineer, probably more wanted in this country than any of the other types.

Now, are we doing our best for our future chemists or for industry by putting them all, together with future school and university teachers, through the same courses of study? Personally I do not think that we are. I shall probably be met by the criticism that there is only one chemistry and therefore there can be but one way of teaching it. Here I disagree, because I feel that the present system leads to the production of narrow specialists, who have not a wide outlook on science generally. In most chemistry schools, especially those of the newer universities, the Honours chemistry course extends over three years, and although classes in physics and mathematics may be a part of the curriculum, this does not of necessity imply any real absorption of these sciences. I am a firm believer in a broad general training in, say, three sciences before the student proceeds to specialise in any one of them; the system, in fact, which used to prevail in the University of London and is still in vogue in a few of our Universities.

Moreover, I do not think the present method of examination is giving us the desired information about candidates or is enabling them to realise what is before them in the future. Far too much is expected from them in the way of book work and far too little in the way of accurate straightforward chemical manipulative skill. Here is what a friend wrote to me the other day, when calling my attention to a really capable young chemist: "My recommendation

is only based upon the possibility of your happening to need a pair of well-trained and capable hands, backed by a mind that is naturally endowed with the scientific curiosity which leads to research. I dare say that, like myself, you have often found that sound scientific training and even brilliant chemical knowledge is sometimes acquired in a University, without the acquisition of any ability to use the hands for sound accurate quantitative work, partly because in some of the University laboratories the value of manipulative skill is not appreciated, and partly because nowadays such an immense amount of theoretical work has to be crowded into the college course that there is little time for the humble utilitarianism of routine analytical operations, though the accurate acquisition of facts is not less important than the projection and co-ordination of the inquiry on which they bear."

I agree with these sentiments entirely and can say with certainty that much has been done to make industry sceptical of the value of trained chemists by the fact that Universities have sent out into the world as first class honours graduates men who could write reams on ill-digested facts concerning molecules, atoms, and sub-atoms, but who had no competency whatever for conducting a straightforward piece of ordinary analytical work. By all means let us give our students a good theoretical grounding and, provided this foundation is sound and on broad lines, the good men will be able to build for themselves upon it, in accordance with the necessities of their future occupations.

I could not attempt to trace here the training that a chemical engineer should be put through, but I do think that everyone going into industry should at all events have some slight knowledge of the subject. Might it not reasonably be made a third subject for a pass degree? I do not by this mean to imply that such a training would be adequate for anyone who wished to become a full-fledged chemical engineer, but it would at all events help a young man going into industry to bridge over the chasm, which exists at present, between the laboratory and works operations. I have often seen a look of astonishment and blank dismay come over the face of a young chemist when he has been shown for the first time a working drawing of a piece of chemical plant. There is certainly no reason why every future industrial chemist should not be taught sufficient of machine drawing and design to enable him to read these drawings with ease.

It must, of course, be granted that there is much, very much, concerning industrial chemistry which cannot be taught in University laboratories and can only be learnt in the works itself, but I think it should be possible, with more co-operation between industrialists



and teachers, to make the learning considerably easier than it is at present.

If it be admitted that our training of future industrial chemists is not all that could be desired, can the blame for this state of things be placed on the teachers only? This question can undoubtedly be answered by an unqualified negative, and others may be asked, for example, What have industrialists done to co-operate with the teaching profession in the training of young chemists? Have industrialists offered any slight advantages to students during their training, or have they in any way made clear their wants, and have they helped as far as possible in making their wants practical possibilities? It would appear that little has been done in any of these directions, and the idea is still prevalent among many industrialists that "the young man who grows up with the business will acquire all the knowledge he needs."

In these circumstances it is an encouraging pleasure to record the fact that the Managing Director of the British Dyestuffs Corporation forwarded in July, 1925, for the information of your President, a copy of a letter which had been addressed to Professors at the various Universities, pointing out that the progress of the synthetic organic chemical industry in Britain depends so largely on the achievements of British chemists, both within and without the industry, and is a matter of such national importance that the most sympathetic co-operation is necessary between the Universities, Technical Schools, and the industry. The letter then invites co-operation in several ways, such as advising the Corporation of likely students for research departments or works processes; giving early notice of laboratory researches likely to have an industrial application; allowing students to carry out researches in conjunction with the Corporation, etc. Finally came the information that the question of permitting a limited number of students to gain works experience with the Corporation during the long vacation was receiving sympathetic consideration, so sympathetic, in fact, that the suggestion materialised and I believe some fifteen students were given, during the summer vacation of 1925, the opportunity of acquiring knowledge in the works of the British Dyestuffs Corporation. The result from the students' point of view was an unqualified success and can scarcely have been a failure from the point of view of the Corporation, since this body is again granting similar facilities to students this summer. The warm thanks of all interested in the training of industrial chemists may be given to the Corporation for this example of the co-operation which is so greatly needed, and for so definitely disproving what in the past was frequently stated to be an impossibility, owing to the dis-

organisation of works practice that it would cause, and also to the danger of works secrets leaking out. If such difficulties have arisen in the present case, it is obvious that the Corporation is willing to face them in view of the importance of the whole question.

In his address last year Professor Wynne directed attention to the desirability of such experience being made possible for students, and stated that in Sheffield the problem had been faced and solved, since it is now the custom for intending graduates in Metallurgy to spend part of the long vacation in certain of the steel works in Sheffield, to be welcomed there and to be placed under foremen to do such work as may be suggested. Now we have the proof that such a state of affairs is not an impossibility in chemical works, and it is to be hoped that the important example set by the British Dyestuffs Corporation will be largely followed by other firms.

Much has been heard recently of the necessity of co-operation between employer and employed, but there is at least as much need for co-operation between business men and teaching institutions regarding educational matters. No one can afford in the interest of our national welfare to say that he has no interests in education, for it is an essential part of the life-work of everyone.

This nation possesses, in addition to others, two most powerful assets which individually have reached great heights. I refer to practical industrial experience and scientific research capacity. If these two forces can be linked together, if the exponents of each can be brought into intimate contact and will in every way possible heartily co-operate with one another, then there is no reason to be pessimistic about the future, for the possibilities such a co-operation opens out are unlimited.

And now, in conclusion, I would express to the Officers, Council, and Fellows of the Society my great appreciation of their kindness to me during my term of office and my deep regret that I have not been able to complete the usual period of two years. I can only say that my interest in the Society has not waned and that I hope in the future to be able still to be of service to the Society.

I should like to add a very special word of thanks to the permanent officials of the Society with whom I have now worked uninterruptedly for 21 years: to Mr. Carr and to Mr. Clifford my sincere thanks are due for the willing and pleasurable way in which they have co-operated with me: and I should also like to thank Sergeant Holland for the share which he has taken in helping me with the work of the Society.

## OBITUARY NOTICES.

## JOHN YOUNG BUCHANAN \*

BORN FEBRUARY 20TH, 1844; DIED OCTOBER 16TH, 1925.

JOHN YOUNG BUCHANAN was born in Glasgow on February 20th, 1844. He was the second son of Mr. John Buchanan of Dowanhill and the elder brother of the Right Hon. T. R. Buchanan, M.P., who represented Edinburgh in Parliament for many years. He was educated at the Glasgow High School and the University of Glasgow, where he graduated in Arts in 1863. His attention had been turned to Chemistry, and he proceeded to study this science on the Continent, spending several years in Germany at the Universities of Marburg, Bonn, and Leipzig, and going on in 1867 to Paris, where he worked in the laboratory of Würtz, a master for whose scientific genius and personal kindness he always cherished a warm admiration.

Shortly after his return to Scotland Buchanan was appointed Assistant to Professor Crum Brown, then recently established in the Chair of Chemistry in the University of Edinburgh, and in 1870, on Crum Brown's nomination, he was elected a Fellow of the Royal Society of Edinburgh.

When the voyage of H.M.S. *Challenger* was planned for the purpose of investigating the physical and biological conditions of the great ocean basins, it was decided that one representative of the physical sciences should be charged with all matters concerning physics, chemistry, and geology, except such hydrographical and meteorological observations as had been assigned to the naval officers. Buchanan was chosen for this comprehensive post by the Circumnavigation Committee of the Royal Society, who had prepared the programme of scientific work. His selection was due largely to his skill and resourcefulness in devising and making apparatus, his reputation as a practical chemist, his knowledge of mineralogy, and his interest in all natural phenomena. The wisdom of the choice was fully justified. Five years were entirely occupied by the *Challenger* work; the preparations for the cruise, and the fitting up of a chemical laboratory in the small space available on board, taking up several months before the ship sailed in December 1872, and the completion of work in hand occupying a longer time after the ship returned in June 1876.

Throughout those years Buchanan's mind was bent on the practical

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problems arising in the study of sea-water; but he took full advantage of the many opportunities for excursions into little-known lands when the ship was in port, and he acquired a love of travel that never left him.

He returned to Edinburgh and set up a private laboratory, in which he carried on research on his own account. The possession of ample means made it unnecessary for him to seek any professional appointment, and he continued to spend much of his time at sea. He made investigations on the west coast of Scotland and on the lochs of the Great Glen in his steam yacht, the *Mallard*; and he took part in several voyages of the cable-laying ships of the Silvertown Company on the west coast of Africa and across the Atlantic, mastering the new methods of sounding by wire, which superseded the clumsy processes of the *Challenger*.

In Edinburgh he entered into the remarkable revival in the study of physical geography and kindred sciences which was a feature of the eighth decade of the nineteenth century, and he took a share in establishing the Ben Nevis Observatory, the Scottish Geographical Society, and the Scottish Marine Station. He contributed a large quantity of material for the equipment of the Physical and Chemical laboratory of the original Marine Station at Granton in 1884, and the writer of this notice had many opportunities there of profiting by his instruction in the arts of observing and recording. In 1887 the Royal Society of Edinburgh awarded the Keith Prize to Buchanan for his work in chemical oceanography, and in London the Royal Society elected him a Fellow.

Buchanan was on terms of friendship with Professor Robertson Smith, who encouraged him in the study of physical geography, and helped to persuade him to accept the lectureship in Geography in the University of Cambridge in 1889. Buchanan was given the Cambridge degree of M.A., and took rooms in Christ's College, where Robertson Smith was already established. He resigned the lectureship after holding it for four years, but Christ's College continued to be his home for twenty years, and in his will he left substantial proof of the regard he entertained for it. On leaving Cambridge, Buchanan took up house in London; but he was much abroad, frequently visiting South America, where he had property in the Argentine, and staying at continental resorts, where he had many friends, some of them in very high positions. Kindred tastes cemented a close friendship with Prince Albert I. of Monaco, and he spent much time as the Prince's guest on shore and afloat, making many cruises in the Mediterranean, the Atlantic, and to Spitsbergen in the Prince's yachts, which were splendidly equipped for oceanographical research.

The outbreak of war in 1914 was a blow from which Buchanan never recovered. He had been on terms of personal friendship with the Kaiser and other distinguished Germans, while his old scientific associations with France had been strengthened by his membership of the governing body of the Oceanographical Institute, founded by the Prince of Monaco in Paris. In real distress of mind, Buchanan gave up his London house and betook himself to Havana, in the West Indies, until hostilities ceased.

His last work was the preparation of three volumes, published by the Cambridge University Press, containing reprints of those of his papers which appeared to him the most worthy of preservation. To these he prefixed very copious analytical Tables of Contents, with comments and criticisms often of great interest. The volumes were: *Scientific Papers*, vol. i.—*Oceanographical*, published in 1913; *Comptes Rendus of Observation and Reasoning*, in 1917; and *Accounts Rendered of Work Done and Things Seen*, in 1919.

After his return to London in broken health, the isolating shadow of old age fell on him, and he withdrew more and more from the society of his remaining scientific friends. He died at the age of eighty-one, on October 16th, 1925.

Buchanan's scientific work was directed to the elucidation of practical problems presented to him during the voyage of the *Challenger*. He did not care for theoretical deductions or comprehensive generalisations. He seemed to work mainly for the satisfaction of his own mind, for once a definite result was obtained the problem lost its driving power; and only a portion of the notes which he amassed, with a care and precision that can only be described as meticulous, was ever worked up for publication. He used to say that he loved work but hated writing; still, the number of his published papers exceeds one hundred.

On the *Challenger* most of his time was filled by a routine prescribed by the Circumnavigation Committee, but the tedium was lightened by flashes of discovery. One was the fact of large concretionary deposits of manganese peroxide produced by chemical action of sea-water on minerals. Another was the discovery that the gelatinous substance found on all preserved deep-sea deposits, which Huxley had taken for a primeval organism and named *Bathybius Haeckeli*, was really a precipitate of calcium sulphate thrown down from sea-water by the addition of alcohol.

The short stay of the *Challenger* in Antarctic waters raised the question of the formation and melting of sea ice, on which Buchanan worked with great keenness for several years, producing a series of valuable papers on "Ice and Brines," in which he worked out the chemical and thermal changes accompanying the freezing of saline

solutions and the temperature at which pure ice melted in them. This led to a further series of calorimetric researches on "Steam and Brines."

Another subject raised on the *Challenger* and settled in a shore laboratory, was the compressibility of glass and other substances under the pressure of the deep sea, ranging up to 5 or 6 tons per square inch. The apparatus invented for this purpose was handed over to Professor P. G. Tait, and used by him in determining the pressure corrections of the *Challenger* thermometers.

Buchanan's most important contribution to the *Challenger* Reports was a memoir on the "Salinity of Ocean Water," in which he published the first complete map of the world-wide distribution of surface salinity, the main features of which have been fully confirmed by later investigators.

His work on the Telegraph ships resulted in a study of continental slopes and oceanic shoals, which had scientific as well as practical value. One of his few general papers was a suggestive survey of Similarities in the Physical Geography of the Great Oceans, contributed to the Royal Geographical Society in 1886. In Limnology he was the first to prove that vertical circulation set up by the wind produced a winter temperature of the deep water in a lake far below the maximum density point.

The work of Buchanan was that of a pioneer breaking new ground, and it was his fate, which he recognised and perhaps resented, to make observations of fundamental importance, which were lost sight of under the superstructure raised by others whose names are better known to the scientific public. All he did was original work in the fullest sense. He owed nothing to other workers. He insisted always on going to the fountain-head, preferably by direct observation, for all data, and on handling such data in the way most likely to ascertain their true relationships even if that required difference from recognised authorities.

His character exhibited singular sincerity, and a kindness which he did nothing to advertise. Although to acquaintances his manner may often have seemed cold and distant, his nature showed a very warm and friendly side to the few congenial comrades of his choice.

H. R. M.

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### GIACOMO LUIGI CIAMICIAN.\*

BORN AUGUST 27TH, 1857; DIED JANUARY 2ND, 1922.

GIACOMO LUIGI CIAMICIAN was the son of Giacomo Ciamician and Carolina Ghezzeo and was born at Trieste, where his father's family,

\* Translated by Sir Wm. J. Pope.



*G. Ciurcian*

[To face p. 996.]







of Armenian origin, had not been long established. The family claimed descent from the great 18th-century historian of the Armenian people, Michele Ciamician.

Ciamician received his secondary education in his native Trieste, where Prof. Augusto Vierthaler initiated him into chemistry; he then studied at the Polytechnic and the University of Vienna, devoting himself principally to Chemistry under Professors Barth and Weidel. While still a student he busied himself enthusiastically and with no little insight upon biological and physical investigations and published several papers of importance, thus laying the foundation of that broad appreciation of physical and biological science which became so evident in his later scientific work and which set the stamp of character on his future triumphs. In 1880 he became a Doctor in Philosophy in the University of Giessen and in the same year was appointed assistant under Stanislaw Cannizzaro in the Institute of General Chemistry of the University of Rome. While in Rome, where he remained until 1887, he was appointed to a Readership, and in this capacity delivered, first, courses of lectures on spectroscopy and, later, on the nitrogenous organic compounds. In 1887 he was chosen in competition for the post of Professor of General Chemistry in the University of Padua, and in 1889, again competitively, he was elected into the corresponding chair in the University of Bologna; here he remained until his death, giving two courses, those of general and inorganic chemistry and of organic and biological chemistry.

The scientific work of Ciamician can be classified in six large groups:

1. *Various Chemical and Physical Investigations carried out between 1877 and 1880.*

This group comprises ten memoirs which deal particularly with spectrum analysis, and also with the resins and the composition of Dippel's oil; it treats of work done in the Polytechnic and the University of Vienna before its author proceeded to his Doctor's degree. The contributions to spectroscopy are of the greatest interest, presenting as they do a comparative study of the spectra of homologous elements which belong to the same group in the periodic system. Ciamician foresaw much that has been since firmly established by more modern methods; he affirmed the spectroscope to be the instrument destined to elicit information concerning atomic motion, and declared that analogous elements of the natural system have analogous structures. These conclusions were far in advance of their time, and it is small wonder that even Mendeléev and Wm. Ostwald judged them as fanciful.

## 2. *The Study of Pyrrole and Allied Compounds.*

This group includes about eighty papers published between 1880 and 1905; therein are described many derivatives of pyrrole with the details which establish the chemical character and behaviour of this base. The aromatic nature of pyrrole and its analogies with the phenols are here developed; these are questions of prime importance in connexion with this group of compounds and later became fundamental to the study of chlorophyll and hæmatin. The reduction products of pyrrole, pyrrolylene, and more especially of pyrrolidine, prepared for the first time in 1885, call for particular mention in that these groupings form part of the nuclei of such important alkaloids as hygrine, nicotine, cocaine and atropine, and of the proteins.

The results of these investigations were collected in a monograph "*Il Pirrolo e i suoi Derivati*," published in 1888, which gained for its author the Royal Prize of the Accademia dei Lincei. Ciamician gave a masterly review of the whole subject in an address to the Deutschen Chemischen Gesellschaft "*On the Development of the Chemistry of Pyrrole during the last Quarter of a Century*," in 1904 (*Ber.*, 1904, **37**, 4200). Amongst the work done in this field should be noted the discovery and utilisation of tetraiodopyrrole or *iodol*, which has found considerable therapeutic use as a substitute for iodoform. To be remarked also is the preparation from pyrrolidine of butadiene, a hydrocarbon which later became so important in connexion with the synthetic manufacture of indiarubber. Meyer and Jacobsen ("*Lehrbuch der organischen Chemie*," 1920, **2**, 147) refer to this group of investigations in their statement—"Das eigenartige Verhalten der Pyrrol-Körper wurde besonders durch eine grosse Reihe von trefflichen Untersuchungen beleuchtet, welche man dem italienischen Forscher Ciamician und seinen Schülern verdankt."

## 3. *Researches on Certain Vegetable Components.*

Thirty-seven papers are devoted to this subject and appeared between 1888 and 1899. The constitutions of a number of organic compounds of vegetable origin were established by these investigations. The work on apiole, and the conversion of safrole and eugenol into their isomerides, which was vital to the industrial manufacture of heliotropin and vanillin, here call for mention; so also does the study of the components of the Coto and similar barks, of pseudo-pelletierine and the constituents of the essential oil of celery, in which the constitution of the aromatic principle, sedanolid, was elucidated. This was one of Ciamician's finest pieces of work; it

preceded that of Willstätter, who developed with such success, and in a variety of directions, the line of investigation so well marked out and defined by Ciamician.

#### 4. *Researches on the Chemical Action of Light.*

Forty notes and nine memoirs were published between 1900 and 1915 on this subject, which was developed into the first systematic study of the behaviour of organic substances towards light.

These researches on the action of light were initiated by Ciamician at Rome in 1886 by his investigation "On the conversion of quinone into quinol by light" and "On the action of light on nitrobenzene in alcoholic solution." They were resumed actively in 1900 and carried on until 1915 in conjunction with Dr. Paolo Silber, who had collaborated in most of Ciamician's work since 1882. The war interrupted this partnership, which is one of the longest, the most fruitful, and the most disinterested joint efforts in chemical scientific investigation. In the course of this work the following photochemical reactions were discovered: the reciprocal reduction and oxidation of alcohols and carbonylic compounds such as aldehydes and ketones, the reduction of aromatic nitro-derivatives by alcohols and aldehydes, the polymerisation of unsaturated compounds and their isomeric changes—this was extended also to the oximes—the hydrolysis of open- and closed-chain ketones, and also of *cyclohexanone* and its derivatives, of menthone, of camphor, and of fenchone, the condensation of hydrogen cyanide with ketones and aldehydes, the aldol condensation of alcohols and ketones, and the synthesis and autoxidation of  $\gamma$ -diketones.

The earlier portions of this series of studies were summarised in a brilliant lecture "On the Chemical Action of Light," delivered before the French Chemical Society in 1908. The later publications on photochemistry treat of the autoxidation of organic acids and of ketones, of bases such as piperidine and nicotine, and of the reduction of copper salts by acetic and benzoic aldehydes. As of especial interest in connexion with autoxidation may be noted that of the *cyclohexanones*, which yield dicarboxylic acids and the corresponding ketones by opening of the ring, and that of oleic acid, in which the double bond is broken, giving a series of lower fatty acids and providing an explanation of the occurrence of rancidity.

During his researches on light as a chemical agent, Ciamician acquired the conviction that the future of organic chemistry lay in its application to biological chemistry and that the more the chemist makes his methods approximate to those of natural pro-

cesses the better he will succeed in elucidating the secrets of nature. Ciamician was never interested in making new compounds for their own sake; he held in horror those substances which only figure in Beilstein, and his work followed no fashion, but was always directed towards the solution of fundamental problems. Plotnikov, impressed by the mass of work carried out by Ciamician and Silber since 1900, has stated that this year marks the basic date in the history of photochemistry.

#### 5. *Researches on Vegetable Chemistry.*

This group of studies is described in nine notes and twelve memoirs and was initiated by Ciamician in 1908 in collaboration with his assistant, Dr. Ciro Ravenna, now Professor of Agricultural Chemistry at Pisa, and was continued until a few months before his death. The problem involved was that of the origin and the functions of the vegetable glucosides and alkaloids.

These investigations constitute a broad and happy attempt to elucidate the functions and mutual transformations of the substances contained in the living plant; its most valuable result has been the synthesis of glucosides by introducing the aromatic compounds concerned into the plant. Thus, salicin is formed as a result of inoculating growing maize with salicyl alcohol. Further, on introducing nitrogenous substances, and especially amino-acids, into plants which produce alkaloids, the production of the latter is increased: thus, asparagine increases the formation of nicotine in the tobacco plant. In another series of experiments, the influence of certain organic substances on the germination and development of plants was studied with a view to ascertaining the function of the alkaloids. From all this work it appears to be indicated that such accessory products as alkaloids, produced in the living plant, are not excretory products, but exercise a function which may be similar to that of the hormones in animals.

Ciamician summarised his work and its conclusions in an elegant and lucid address "On the Biological Significance of Alkaloids in Plants," delivered in October, 1921, at the meeting in Trieste of the Italian Association for the Advancement of Science. This was the last occasion on which he spoke in public, and he concluded the account of this very beautiful piece of synthetic work by stating—"The conclusion deduced from what we know at present, is that the plant practises a chemistry corresponding to that practised in the laboratory, but does so by means infinitely more simple than ours, although with objects similar to ours. The plant organisation is less differentiated than that of animals, and volitional manifestation is less developed, but amends are made

by the exercise of a highly perfected chemical technique; the plant consciousness is a chemical consciousness."

6. *Memoirs and Notes on Physical Chemistry.—Addresses and General Discourses.*

The first work of Giacomo Ciamician was on physical chemistry, and he continually followed the development of this science; indeed, he made notable contributions to it by a few but fundamental papers. The note "On a Lecture Experiment for Demonstrating Raoult's Law," and that "On the Theory of Electrolytic Dissociation," in which he was perhaps the first to advance the idea of complexes formed between the ions and the molecules of the solvent (*i.e.*, solvates of the ions), are worthy of remark. Again, the paper "On the Relations between the Chemical Constitution and the Property of forming Solid Solutions of Organic Compounds" was the starting point of fruitful investigations in his own laboratory and culminated in the classical work of Bruni on solid solutions. The note on "Considerations on the Nature of Chemical Affinity and of the Valency of the Atoms," published with Padoa in 1918, came early in the introduction into our science of the electronic constitution of the atom, and some of the views put forward are really profound and merit further development now that the secrets of atomic constitution seem in the main unveiled. Ciamician's point of view in the treatment of questions of general interest was a very admirable one. In his inaugural address on "Chemical Problems of the New Century" in 1903 he showed a real gift for the dignified but at the same time efficient popularisation of science; this power was still further developed in a lecture on "Problems and Objects of Modern Organic Chemistry," given at Vienna in 1907, in those on "Organic Chemistry in Organisms" at Parma in 1908, and on "The Co-operation of the Sciences" at Naples in 1910, and, lastly, in his magnificent discourse on "The Photochemistry of the Future," read at New York in 1912 before the 8th International Congress of Applied Chemistry. In this sparkling address he developed many fundamental conceptions which have been taken up in numerous later well-known utterances by others; he insisted on the need for setting plants to work, so that we may conserve, so far as may be possible, our natural wealth of fossil fuels, which is really small, and of applying photochemistry in desert regions to the utilisation of the solar radiation.

"On the arid earth," he says, "will spring up industrial colonies without soot and without chimneys: forests of glass tubes and greenhouses of all sizes will rear themselves before the sun, and in this transparent apparatus will proceed those photochemical

processes of which the secret and the monopoly are at present held alone by the plant, but which human industry will learn how to wrest from it. That knowledge will be usefully applied in quite new ways, because whilst nature is incapable of haste, humanity can act more speedily; if, in some distant future, the moment arrives when fossil carbon becomes exhausted, it will not entail the death of civilisation, for life and its amenities will endure so long as the sun shines." He took up this argument again, and in a form which appealed to a larger public, in his article on "Chemical Industry without Carbon," published in the "Nuova Antologia" in 1917.

Amongst other writings of Ciamician which call for special mention are those devoted to the memory of Stanislao Cannizzaro and of his intimate friend Augusto Piccini, and the discourse, pregnant with thought, delivered at the celebration of the 70th birthday of Guglielmo Koerner.

The vast output of scientific work of outstanding merit produced by Giacomo Ciamician has been very briefly summarised in the above pages; it appears the more remarkable by contrast with the penury of his laboratory, which made his work a real struggle. He was an incomparable master in the laboratory and the lecture theatre and a great stimulus to energetic work. His numerous pupils now fill the most important chairs of chemistry in Italy and hold high the renown of Italian chemistry; amongst them may be mentioned Angeli, Magnanini, Plancher, Garelli, Bruni, Mascarelli, Ravenna, Boeris, Cambi, Barbieri, Padoa, and Ciusa, together with Zanetti and Rimini, who have passed away. He initiated and vigorously inspired much original work which did not come strictly within his own field; thus arose the investigations of Bruni, Garelli, and Padoa. Himself indefatigable, he inspired in all a noble enthusiasm for assiduous work. His lectures, to which he devoted himself like an apostle, were models of elegance, of precision, and of vivacity, as well as in the choice of experiments; they were one of his great passions, and it was always for him a sad day when he could not appear before his class, which welcomed him with growing applause, repeated at the close of the lecture. Against the advice of his friends and students, and when already attacked by fever in November 1921, he wished to commence his courses in general and in organic chemistry; immediately afterwards he was laid aside by the insidious malady which took him from us.

Giacomo Ciamician was a member of practically all the Italian Academies and scientific bodies, as well as of a large number of foreign societies. He had been President of the Italian Society for the Advancement of Science and of the Italian Association for Pure and Applied Chemistry; he was an honorary member of the

English, French, German, and American Chemical Societies, and a foreign member of the French Academy of Sciences. He was an honorary LL.D. of the University of Glasgow and an honorary member of the Royal Institution of Great Britain. He did not seek dignities, but he was a Cavaliere dell' Ordine del Merito civile di Savoia and a Chevalier of the Legion of Honour. After 1910, he worked actively as a member of the Italian Senate. He had a distaste for militant politics, but nevertheless his voice did not fail the Senate when questions arose which concerned education or the chemical industries; his principles were broadly liberal and he was greatly attached to his native Trieste. Immediately after his graduation he left Vienna, although he could have found there an ample career and ample means for carrying out his work, and came to Italy. At the death of Professor Weidel, an occasion offered for his election as Professor in Vienna with honours, means of work, and emoluments far greater than those he enjoyed in Italy; notwithstanding his gratitude to his former teacher, Professor Lieben, he never thought for a moment of abandoning Italy.

During the war he devoted his great abilities with much self-sacrifice but with juvenile enthusiasm to the work allotted to him; this work was arduous and intense and, whilst without doubt valuable to our country, undermined his already shaken constitution. Towards the end of the war he was smitten by two great sorrows, first, the death of his mother and later that of his dearly-loved sister, Carolina, the wife of Professor R. Nasini. The last great pleasure of his life was to witness the liberation of his native Trieste. Trieste had always held him in affection and esteem as one of the elect of her sons, and decided on his death that the Via degli Armeni, in which is the house of his aunts on the mother's side where he passed his youth and which he made his home when in Trieste, should be renamed the "Via Giacomo Ciamician." On the house in which he was born, 21 Via S. Martiri, the Municipality has placed a bronze medallion with his portrait and an inscription by the well-known patriot and scholar, Senator Attilio Hortis.

Ciamician was of a benign and fine presence; his blue eyes expressed his great kindness and revealed the simplicity of his nature; he was easily moved to anger, but incapable of harbouring offence. He had a genius for friendship and lavished a noble affection upon his intimate associates; he was simple and upright in private life and a model of the civic virtues. His mind was open to all the great modes of intellectual expression; amongst the arts he loved above all that of music, and in this, even in musical Bologna, he was considered as one of the highest authorities. The Queen Margherita held him in affection and enjoyed his thoughtful

and animated conversation; he had friendships amongst all the chief chemists of his day, more particularly with Emil Fischer, who several times proposed him for the Nobel prize, with Albin Haller in France, and with Henry E. Armstrong.

Bologna was proud to look upon him as one of her citizens and followed anxiously the vicissitudes of his last illness, an insidious malady from which so rapid an end was not to be foreseen. He passed away quietly in the arms of his brother-in-law, Professor R. Nasini, and of his nephew, Dr. A. G. Nasini, and surrounded by his relatives from Trieste; most of his former students had collected in Bologna to be present at the end. They took part in the last solemnities when he was laid to rest on a cold and bright January day; to the accompaniment of Beethoven's funeral march, as Ciamician had wished, the great procession passed among the mourning populace through the streets of the old turreted city he had loved so well.

A memorial stone has been placed by his students on the house which he had always occupied, No. 3 Via Guido Reni. In a short time the new Chemical Institute will be inaugurated; Ciamician had devoted much of his activities to this project and its execution and hoped much from its future. It will carry on its façade the inscription "Istituto Chimico Giacomo Ciamician." An honour worthy of the great man of science.

RAFFAELLO NASINI.

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### SAMUEL HENRY DAVIES.

BORN SEPTEMBER 19TH, 1870; DIED MAY 9TH, 1925.

SAMUEL HENRY DAVIES was born at Liverpool on September 19th, 1870, the son of Richard Davies, pharmacist. He received his early schooling in Liverpool, and was then for four years at the Friends' School at Sidcot in Somerset, where he already showed a keen interest in chemistry. He studied successively at University College, Liverpool, and Owens College, Manchester, and graduated B.Sc. at Manchester in 1890 (M.Sc. in 1893), winning a scholarship which took him to Heidelberg. Here, under the direction of Victor Meyer, he carried out a research on "Alkyl and Acetyl Sulphides," which was published in the *Berichte* in 1892, and a minor research with Emil Feith on the "Action of Hydroxylamine Hydrochloride on Acetomesitylene."

After returning to England Davies held university posts as demonstrator first at Manchester and later at Leeds, and won the esteem of professors and students. His professor at Leeds says: "I never parted with a demonstrator more reluctantly, for



he was an excellent teacher full of life and go, ready to take up and carry out any promising new plans of instruction."

In 1893 Davies was appointed the first head of the chemical department at the new Battersea Polytechnic; into the organisation of this department he threw himself with whole-hearted and characteristic energy. Here he remained until in 1896 he was appointed chemist to Rowntree and Co. at the Cocoa Works, York. This post he held for more than twenty-five years, during which the original small laboratory with one assistant grew under his direction to a finely-equipped department with a staff of fifty.

Davies was a man of the widest human sympathies and his work at York did not end with his duties as chemist but covered a varied field; he lived a very full life both in the works and in the city. He took the keenest possible interest in the welfare of the workers and in their various clubs and social activities, devoting much time in the earlier days to the swimming, rowing, and football clubs.

In 1907 Davies married Miss Edith M. Oliver and about this time was elected a member of the York City Council, on which he represented Castlegate ward for nine years. He was a strenuous advocate of the feeding of necessitous school children and of a clean milk supply and was the author of pamphlets published by the York Health and Housing Reform Association.

Much of Davies's work for the firm could not be made the subject of publications, but in 1904 he published (with McClellan) a paper on the amount of fat contained in cocoa beans of different origin and in 1912 (with J. S. Bainbridge) a valuable paper on "The Essential Oil of Cocoa." He directed much attention to the general problems of factory working, and papers published in 1903-1904 on the "Relative Efficiency of Insulating Media" embody the results of detailed research on the comparative value of materials used for covering steam-pipes. He also wrote on factory ventilation and lighting and devised a simple and rapid method for the estimation of carbon dioxide in the atmosphere.

On behalf of Rowntree and Co. Davies made journeys in many countries, notably in South America and the West Indies; he returned to the West Indies several times in connection with the development of Rowntrees' estates. He always maintained his interest in these islands and was a prime mover in establishing the Technical College in Trinidad, of which he was appointed a governor.

Davies was a member of the Fell and Rock Climbing Club and, an enthusiastic lover of mountains, spent many summer holidays in the Tyrolean Alps.

From 1919 Davies suffered from ill-health and after a break-

down in 1922 relinquished his full time duties at the cocoa works, but was still retained by the firm as consultant. He built himself a new home and a laboratory at Jordans in Buckinghamshire, where he intended to continue research work, but his health broke down completely and he passed away on May 9th, 1925.

Davies possessed an unusual charm of manner and disposition and was beloved by a wide circle of friends; excellent chemist as he was, chemistry was to him but one means of approach to his fellow men. A writer in the *York Gazette* says of him: "When S. H. Davies saw something to be achieved which could bring gladness and essential prosperity into the lives of his neighbours, he sought for this with his whole soul and strength, however strong and influential the forces against him," and one who worked with him in his later years rightly described him as "gentle and charitable, indulgent to others, severe to himself and unwearying in service to friends." His was a noble nature and we who knew him are sorrowful that he has left us so soon.

REGINALD BROWN.

### WILLIAM HENRY DEERING.

BORN DECEMBER 19TH, 1848: DIED SEPTEMBER 5TH, 1925.

WILLIAM HENRY DEERING was the youngest son of W. Deering of Gravesend. He received his early education at the City of London School and in 1864 entered the College of Chemistry as a student under Hoffman. After short periods as assistant to Sir Benjamin Brodie at St. Bartholomew's Hospital and with William Odling at Oxford, in 1867 he joined the staff of Sir Frederick Abel, Chemist to the War Department, at the Royal Arsenal, Woolwich. He spent the rest of his life, until his retirement in 1909, in the Government service, becoming himself Chemist to the War Department in 1905.

Like that of many other civil servants, Deering's work was unknown to the general public, but he played no small part in the application of chemical science to military materials which showed so remarkable a development towards the end of last century. Although the introduction of cordite is associated with the name of Sir Frederick Abel, the fundamental researches which led to its adoption in the British Service necessarily depended on his assistants, and of these Deering and his colleague, the late William Kellner, were mainly responsible for the work. It is sufficient testimony to the thoroughness and completeness of their labours that, in spite of continuous efforts to improve upon it, the cordite of to-day is substantially the same as that introduced into the Service in 1889.

In addition to his work on cordite, Deering was called upon, in the course of his long service, to deal with a large variety of chemical and physical problems in connexion with explosives and other military stores. He carried out much important investigation in perfecting electrically-fired detonators for use in the field.

As regards contributions to the literature of their profession, scientific officers of the public service suffer from certain disabilities. It frequently happens that their more important work is of a confidential nature, or, if not, that it is published in the form of a report by the Head of the Department, in which the part played by individuals is not shown. To these facts, coupled with Deering's marked distaste for publicity, is due the relatively small number of papers under his name. Perhaps the most important are those (with Abel) on the conditions in which carbon exists in steel (J., 1883, 43, 303) and (with Kellner) on the measurement of pressure by the crusher gauge (*Proc. Roy. Soc.*, 1895, 57, 404). But he also contributed papers to the Society's *Journal* on water analysis and on lead salts, and to other journals on mineral oil and certain fatty oils. He was responsible for the article on "Explosives" in the first edition of Thorpe's "Dictionary of Applied Chemistry" and received a medal for a lecture on the same subject before the Royal Society of Arts.

Deering's knowledge of chemical literature was encyclopædic. He remained a student throughout his career and had an exceptionally retentive memory. There were few subjects upon which he could not, without hesitation, refer an inquirer to the more important papers dealing with them. In the laboratory, his work was characterised by meticulous care. He took nothing for granted, satisfied himself at every stage of the accuracy of his work, and eliminated or evaluated every possible source of error. He was a good linguist, speaking French and German fluently. He had also a working knowledge of Italian and the Scandinavian languages.

Inclined to be somewhat impulsive and outspoken, and intensely disliking insincerity of any kind, it was only those who knew Deering well who could realise his kindness of heart. He was incapable of an ungenerous act, and appreciated the work of his humblest assistant.

Deering lived for his work, and the Companionship of the Imperial Service Order, conferred upon him in 1906, was an inadequate recognition of a life of really devoted service to his country.

Deering married, in 1905, Isabel, daughter of Thomas Cowie of Blackheath. Upon his retirement, he moved to Devonshire and, after some years of failing health, died at Torquay on September 5th, 1925.

A. V. E.

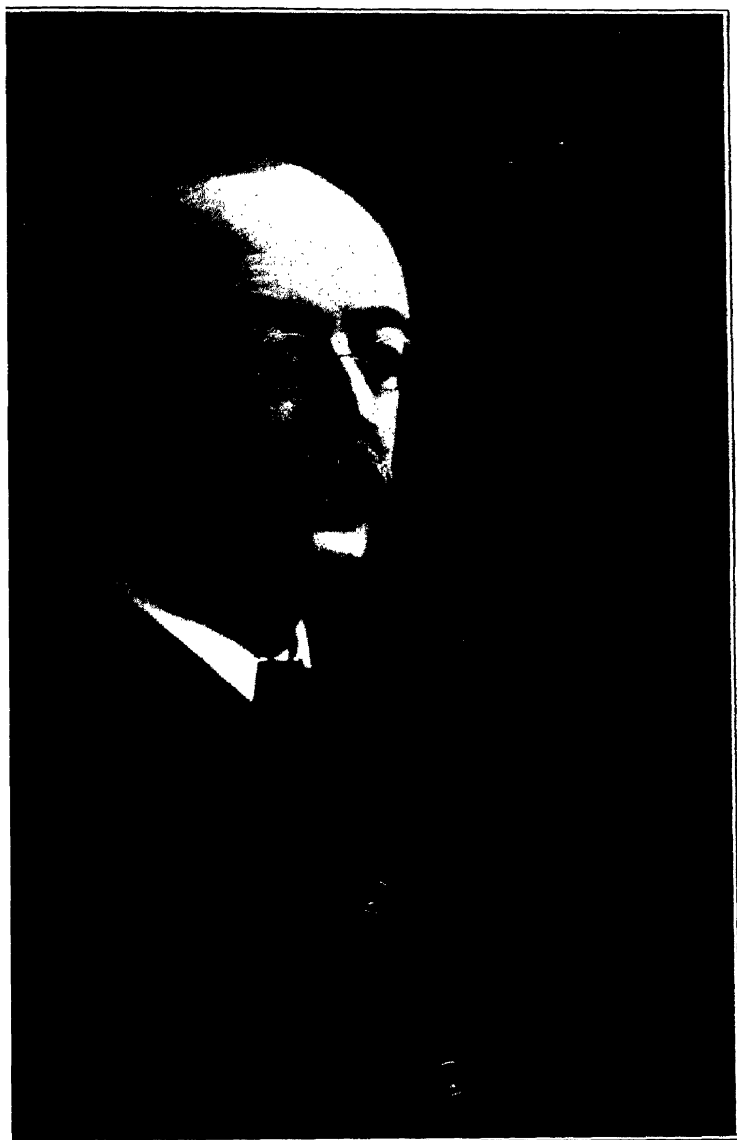
## FRANCIS ROBERT JAPP.

BORN FEBRUARY 8TH, 1848: DIED AUGUST 1ST, 1925.

FRANCIS ROBERT JAPP, a member of a family of Dutch origin, whose name was well-known half a century ago in the eastern districts of Forfarshire, was born in Dundee on 8th February, 1848, the youngest son of James Japp, minister of the Catholic Apostolic Church in that city. His earliest education was obtained in the town of his birth, in part at the High School there; but in 1861, at the age of thirteen, he was sent to St. Andrews, the reputation of which as an educational centre stood then, as now, very high. After three years spent at the Madras College, he entered the University as a student in the Faculty of Arts.

The course of study for the Arts degree extended, at that time, over four winter sessions of five to six months each (there were no summer sessions), and the subjects studied were Latin, Greek, Mathematics, English, Logic and Metaphysics, Moral Philosophy, and Natural Philosophy. While at St. Andrews, Japp contracted a lifelong friendship with John Masson, essayist and author of "Lucretius, Epicurean and Poet."

After graduating M.A. at St. Andrews, Japp entered the University of Edinburgh in 1868 as a student of law; but his period of study at Edinburgh proved to be a short one. In the summer of 1869 his health broke down and he was compelled to relinquish his legal studies and to reside abroad, at Pau and at other health resorts. For two years, from the spring of 1871 to the spring of 1873, Japp resided in Germany, at Göttingen, Berlin, and Heidelberg; and although, during a portion of that time, he attended lectures on International Law and on German Literature, he had, even then, abandoned his intention of prosecuting the study of law. The record of the following two years will be more interesting if told in Japp's own words, communicated to the writer in a letter some years ago: "In the spring of 1873, I returned to England and spent the time partly in London, partly in Scotland. I had by this time taken up the subject of chemistry, in which I had always been interested. In the autumn of 1873 I returned to Heidelberg and began the study of that subject under Bunsen. I was then twenty-five years of age, and my friends, who had long despaired of my ever taking up anything seriously, regarded this last step as the crowning folly of a hopeless career. In 1875 I graduated Ph.D. at Heidelberg (only *insigni cum laude*). I was anxious to get all examinations behind me as soon as possible and, I fear, rather hurried matters. The Heidelberg Ph.D. at that time required no 'dissertation' and was rather a worthless degree;



Yours sincerely,  
F. R. Japp.

[To face p. 1008.]



there was no practical examination—merely an ‘oral’ of two hours. I stayed with Bunsen until the end of the summer semester, 1876, devoting the winter semester to the separation and preparation of various rare elements and the summer to a rather impossible piece of research which Bunsen had suggested and which led to no result. I also heard lectures by Hermann Kopp, on the History of Chemistry; by Hermann Quincke, on Physics; and by Blum, on Mineralogy. Contemporaries of mine in Bunsen’s laboratory were John Gibson, J. E. L. Shadwell, C. Loring Jackson, W. F. Hillebrand, T. H. Norton, F. P. Treadwell, Charles Otto Trechmann, Hans Jahn, and Siegmund Gabriel.”

From Heidelberg Japp proceeded to Bonn to work in the laboratory of August Kekulé, who had, some years previously, been appointed to the Chair of Chemistry in the University and had attracted to his Institute large numbers of young chemists of different nationalities. Whether the young Scottish chemist felt, as did van ’t Hoff, that the laboratory of Kekulé was a sacred temple to be entered only with feelings of reverence and of awe, we cannot say; but the Memorial Lecture on Kekulé, delivered by Japp in 1897, bears, in its every line, clear and eloquent testimony of the esteem and admiration which he felt for his new teacher, who, although no longer at the height of his physical power, preserved his mental faculties unimpaired and could still inspire work of unsurpassed excellence. It was in the palatial laboratory at Bonn that Japp, under the more immediate guidance of G. Schultz and of Anschütz, first entered on that course of chemical investigation which he pursued with such wholehearted devotion and success for over thirty years. Among Japp’s contemporaries at Bonn were P. Phillips Bedson, Henry Forster Morley, Richard Taylor Plimpton, and Shadwell.\*

\* The writer is indebted to Geheimrat Professor R. Anschütz for the following reminiscences of Japp’s period of study in Bonn:

“Japp wohnte in Bonn mit seiner Mutter in einem Haus in der Kölnstrasse im Nordosten Bonns weit weg von dem in Poppelsdorf gelegenen chemischen Institut. Das beschränkte stark seinen Verkehr mit seinen Studiengenossen, die er nur im Laboratorium sprach; von studentischen Kneipereien hielt er sich fern. . . .

“Damals war Gustav Schultz Kekulé’s Privatassistent und ich Vorlesungsassistent. . . . Soweit es meine Arbeiten für Kekulé gestatteten, arbeitete ich mit Schultz über das Phenanthren. Japp schloss sich an uns an und wir lernten im persönlichen Umgang die liebenswürdigen Eigenschaften des um einige Jahre älteren Fachgenossen schätzen, der nicht nur die deutsche Sprache völlig beherrschte, sondern sogar einen ausgesprochenen Sinn für den deutschen Volkshumor an den Tag legte. . . .

“Da Gustav Schultz und ich unsere Arbeitsplätze neben Kekulé im Privatlaboratorium hatten, so brachte es Japp’s Entschluss mit uns zu

In 1878, Japp returned to Scotland and continued his research work in the laboratory of Professor Crum Brown, Edinburgh. Later in the same year he was chosen by Professor (later Sir) Edward Frankland, out of a large number of candidates, to take charge of the Research Laboratory which was then being established at the Normal School of Science, South Kensington, and to devote his whole time to the supervision of the research students. In 1881, when the Science Schools were reorganised by the Science and Art Department, Japp was promoted to the rank of Assistant-Professor in what was then called the Royal School of Mines and Normal School of Science, and which, at a later date, became the Royal College of Science. Here, under E. Frankland and later under T. E. Thorpe, who succeeded to the Chair of Chemistry in 1885, Japp continued to direct the work of research in, as well as to lecture on, organic chemistry. Although recognised as a brilliant research chemist, Japp felt that he was adversely affected in his candidatures for a Chair by his lack of experience in the conduct of a general laboratory, and in 1889, on the departure of P. F. Frankland to occupy the Chair of Chemistry at Dundee, Japp requested and was given a share in the teaching work of the large laboratories. Unsuccessful in his candidature for the Chairs at Leeds in 1885 and at Dundee in 1889, Japp was appointed to the Chair at Aberdeen in 1890, in succession to Thomas Carnelley.

The twelve years spent in London constituted, perhaps, the "Golden Age" of Japp's scientific life. Filled with an enthusiasm for research, Japp not only found his work at the Normal School (and Royal College) of Science for the most part congenial and satisfying, but he also greatly enjoyed participating in the active scientific life which found its focus in the Chemical Society, at the meetings of which he was often a conspicuous figure. In the discussions which there took place, as the writer is informed, "opportunity arose for his revealing, not only his dry humour, but also his profound knowledge of chemical literature and a width of classical and philosophical reading altogether beyond the range of the attainments of the great majority of his contemporary

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arbeiten mit sich, dass er mit Kekulé genauer bekannt wurde, als es sonst geschehen wäre. Kekulé fand bald Gefallen an Japp's immer bedächtiger aber stets klarer Art sich in der Unterhaltung über wissenschaftliche Fragen auszusprechen.

"Als im Jahre 1878 die Stelle eines Demonstrator der organischen Chemie am Royal College in London bei Frankland zu besetzen war, bewarb sich Japp darum, unterstützt durch ein ausgezeichnetes Zeugnis von Kekulé, und Frankland gab ihm vor anderen Mitbewerbern den Vorzug. Wie mir Japp später mitteilte, habe Frankland besonders unsere Beweisführung der Konstitution des Phenanthrens gefallen."



chemical colleagues." Japp valued also the personal contacts with the leaders and fellow-workers in chemical science which residence in London made possible. On the other hand, Japp's scientific accomplishments, his well-stored and cultured mind, and his remarkable personality won the admiration, regard, and esteem of his fellow-chemists, and he was early called to serve on the Council and the Publication Committee of the Chemical Society. Although, to the great regret of his many scientific friends, Japp seldom, after his departure in 1890, re-visited London or took part in the gatherings of chemists elsewhere, one could not fail to note how, in later years when settled at the northern University, he sometimes looked back with something of wistful yearning to the inspiration and stimulating fulness of life which the Metropolis offered to the scientific worker.

While at the Royal College of Science, Japp gathered round him a large number of able and enthusiastic students, and research was prosecuted with great activity. About half the total number of scientific papers which Japp published, either independently or in collaboration, appeared during his London period.

During this period, also, Japp contributed to the advancement of chemistry by the publication, in collaboration with E. Frankland, of a text-book of Inorganic Chemistry which was "constructed on those principles of Classification, Nomenclature, and Notation which, after an experience of nearly twenty years, have been found to lead most readily to the acquisition of a sound and accurate knowledge of elementary chemistry." The composition of the book was mainly the work of Japp, and the more theoretical sections, such as the chapter on the Atomic Theory, are excellent examples of clear and well-reasoned exposition. Owing, doubtless, to the adoption of Frankland's constitutional formulæ and nomenclature, which did not find favour with contemporary chemists, this work did not have the circulation which it deserved.

Japp also collaborated with Frankland in the preparation of a new edition of the latter's "Lecture Notes on Organic Chemistry."

From the Royal College of Science Japp proceeded, as has been noted, to the University of Aberdeen. He was, perhaps, fortunate in the date of his appointment, for it fell on the eve of a very great and rapid development of the University, marked, not only by the erection of imposing buildings and an increase in the number of its teachers, but also by a renewed activity in literary and scientific investigation. In all this progressive movement the Chemistry Department, under Japp's guidance and enthusiasm, played a notable part.

Until 1896, the Chemistry Department of the University of

Aberdeen was housed in a series of four or five small rooms, badly lit and badly ventilated, which afforded accommodation of a very inadequate character for only two or three advanced students working at one time. Two of the rooms, in which the classes in practical chemistry for medical students were held, were fitted with a circular table without sink and without water-supply other than that contained in a jug placed on the narrow working bench. In these rooms even the most primitive arrangements for the extraction of fumes were wanting, so that when fifteen or twenty students were vigorously boiling off excess of aqua regia, the figure of Japp, seated on a stool in the centre of the space enclosed by the circular work-bench, could be only faintly discerned through a mist of acid vapours.

With such accommodation at his disposal, it was clear that it would be impossible to build up a school of chemistry of any importance, and Japp therefore set about the task of arousing public opinion and of stimulating the University authorities to a recognition of the claims of chemistry to more adequate accommodation. His reward came at last, and in 1896, with the carrying out of a scheme of University extension, Japp found himself installed in laboratories which, at that time, could be regarded as palatial, but which, in the space of thirty years, have become inadequate for the requirements of the present day.

Development, however, took place in directions other and more important than towards new buildings. Previously, the work of the Chemistry Department had consisted, almost entirely, in the teaching of elementary chemistry to medical students, but soon after Japp's installation as Professor at Aberdeen, a Faculty of Science was instituted, courses of instruction leading to the degree of B.Sc. were introduced, and a school of advanced chemical study rapidly grew up. It must, indeed, be regarded as not the least important and valuable of Japp's contributions to the advancement of chemical science that, in an area where there had previously existed no school of advanced chemical training or tradition of chemical study, he created a vigorous school of chemical instruction and research from which there has issued a succession of chemists, many of whom occupy important academical and industrial posts in various parts of the world.

While at Aberdeen, Japp delivered, each year, two courses of lectures, one on elementary inorganic chemistry and one on organic chemistry; and it must be confessed that as a lecturer to young Scottish students, perhaps the most testing audience for any lecturer to address, Japp fell somewhat short of achieving complete success. It may be that he did not sufficiently bear in mind that

the great majority of the students attending his elementary class came to him entirely ignorant of chemistry or were hearing his lectures, not from choice, but under the compulsion of regulations; and it may also be that he was, temperamentally, somewhat out of touch with the mind of the average young student. As a consequence, the generous appreciation of which the Scottish student is capable sometimes degenerated, unfortunately, into an irritating disturbance or even a boorish noisiness. This behaviour on the part of his students was a constant source of annoyance and worry to Japp, and even told adversely on his health. On one occasion, when the disturbance was more than usually bad, Japp was roused to protest. Halting in the course of his lecture, he gazed on his students for a few moments and said: "Gentlemen, I have been a member of four Universities—London, Edinburgh, St. Andrews, and Aberdeen—and I find that the higher the latitude the lower the breeding."

For his comparative lack of success with his elementary class, his success as a lecturer on organic chemistry to advanced students in science must have been some compensation. In this case, the lecturer was dealing with a branch of chemistry to which he had devoted his life and he was in the presence of a serious body of students to whom he gave of his best. Drawing on his wonderful knowledge of the subject and brightening, here and there, the intricacies of a problem in constitution with a touch of personal reminiscence, Japp revealed to his students the main features and course of development of organic chemistry in a manner which, to the student, was most impressive and showed Japp's mastery of detail, clearness of thought, and accuracy of language.

In all his teaching, whether in the lecture room or in the laboratory, Japp was intolerant of haziness of thought and slovenliness of manipulation; and the high standard of clear thinking, accurate expression, and neatness of experimental work which he set for himself and demanded of his students did not fail to make an inefaceable impression on his pupils.

It was, however, in the research laboratory that Japp was most at home and at his best. With the help of a research assistant, maintained by means of a grant from the Royal Society, and in later years with the assistance of his own graduate pupils, Japp was enabled to maintain, although in somewhat diminished volume, his output of research work. During his tenure of the Chair at Aberdeen, upwards of forty papers were published by Japp in collaboration with his private assistants or research students. Although the last paper to bear his name appeared in 1905, Japp continued to inspire and direct the research work of members of

his staff; and, with a modesty approaching almost to self-depreciation, he frequently effaced himself in order that his reputation and seniority might not deprive his younger colleagues of any credit to which they might be entitled. This self-effacement was exhibited, not only in connexion with the publication of research, but also in connexion with the organisation and development of the teaching work of his Department.

Although always jealous of the interests of his Department and active in its development, Japp took no prominent part in University politics or in the general work of administration. Nor did he take much part in the life of the various University Societies. "Whenever they" (the officials of the societies) "came to me for an address, I used to give them a sovereign, which I have no doubt was infinitely more acceptable." This, of course, was not the case, and one cannot but regret, from the point of view of the students, that Japp refrained from making use of the opportunities which offered of impressing on a larger body of the students something of his own remarkable personality, of imparting to them something from his great store of scientific and literary lore, and of encouraging in them the cultivation of the wide and philosophic outlook which he himself possessed. Japp, however, had little of the missionary spirit and no great love for the platform or the market place; and he preferred to share the treasures of his mind chiefly with those who were associated with him in research or had the good fortune to enjoy his friendship.

Commencing, as Japp did, his career as a chemical investigator in the laboratory of Kekulé, who, to quote from the Memorial Lecture, "brought an intellect of incomparable power and subtlety to bear on problems so abstruse, so remote from the everyday thoughts and interests of mankind, that the vast majority even of educated persons have never heard either of the problems or of the man who did so much to solve them," it is, perhaps, not surprising that Japp's research work was by no means "popular." It concerned itself at no point with problems of everyday experience or of immediate industrial importance, but dealt with many difficult problems of chemical constitution which required for their solution greater chemical acumen and a more profound knowledge than is the case with many investigations which make a more direct appeal to the lay mind. Endowed with a very retentive memory, Japp took to heart, and passed on to his pupils, the counsel which Liebig gave to Kekulé: "If you want to be a chemist, you will have to ruin your health; no one who does not ruin his health with study will ever do anything in chemistry nowadays." The *Journal of the Chemical Society*, the *Berichte*, and

the *Annalen* were Japp's constant companions, and the *Jahresbericht* formed his holiday reading. As a result he acquired an incomparable knowledge of organic chemistry which, together with a great capacity for accurate and laborious experimental work, the power of clear thinking and reasoning, and a highly developed "chemical instinct," enabled him to solve successfully many obscure problems of chemical constitution. Japp, moreover, was imbued with the spirit of the true scientific investigator intent only on eliciting the truth, without thought of personal ambition or material gain.

The raw materials of almost all of Japp's research work were phenanthraquinone, benzil, and benzoin; and from a paper (J., 1897, 71, 123) which may almost be regarded as the *apologia* of his scientific life one learns that the main objects of the systematic study of the condensations of the ketones and keto-alcohol mentioned were the synthesis of cycloids and the comparison of the properties of ortho-diketones of the aromatic series with those of the  $\alpha$ -diketones or keto-alcohols of the aliphatic series. As he pointed out: "At that time, Ladenburg's 'prism' formula could still be seriously put forward as a satisfactory expression of the reactions of benzene; and in this formula the ortho-carbon atoms are not directly united. Every condensation, therefore, which bore out the foregoing analogy" (between aromatic and aliphatic  $\alpha$ -diketones) "was a fresh argument against the 'prism' formula. Indeed, it is cumulative evidence of this character, rather than any definite disproof, that has caused the 'prism' formula to be withdrawn from discussion."

It may be remarked that some of Japp's earlier investigations (e.g., J., 1880, 37, 410; 1882, 41, 146), which were undertaken partly with the object of throwing light on the constitution of phenanthraquinone itself, supported Graebe's peroxide formula; later work, however (e.g., J., 1883, 43, 27), furnished a very strong argument in favour of Fittig's formula, which was subsequently always employed.

The success with which the main object of Japp's research work, the synthesis of cycloids, was realised, is well seen from the following list of the various classes of compounds formed in different condensation processes:

*Oxazoles*.—1. By the interaction of  $\alpha$ -diketones with aldehydes and ammonia (J., 1880, 37, 669; 1881, 39, 225). 2. From benzoin and nitriles (*ibid.*, 1893, 63, 469).

*Iminazoles*.—1. *Ordinary (secondary) Iminazoles*.—From  $\alpha$ -diketones, aldehydes, and ammonia (*ibid.*, 1882, 41, 146, 157, 323; 1886, 49, 464; 1887, 51, 552, 557). 2. *Tertiary Iminazoles and*

*Quaternary Ammonium Compounds.* From  $\alpha$ -diketones and primary amines of the formula  $R \cdot CH_2 \cdot NH_2$  (*ibid.*, 1895, 67, 32).

*Furfurans.*—By the action of hydriodic acid on the condensation products of  $\alpha$ -diketones with ketones (*ibid.*, 1890, 57, 662).

*Indoles.*—By the condensation of benzoin with primary benzenoid amines (*ibid.*, 1894, 65, 889).

*Azines.*—By the action of ammonia (1) on benzoin and (2) on  $\alpha$ -diketones (*ibid.*, 1886, 49, 828; 1887, 51, 98).

To the above series of compounds one may also add *lactones*, *pyrrolones*, and *pyrroles*.

In addition to the foregoing classes of compounds, all of which are heterocyclic, a number of pentacarbon ring compounds were also synthesised. Chief among these are *anhydracetonebenzil*, obtained by the condensation of benzil with acetone (J., 1885, 47, 21); *anhydracetonebenzilcarboxylic acid*, by the condensation of benzil with acetonedicarboxylic acid (J., 1897, 71, 139); and two isomeric *anhydrobenzil-lævulic acids*, by the condensation of benzil with lævulic acid (J., 1897, 71, 144).

For the most part, the superstructure of Japp's synthetic work was founded on a new reaction which he discovered, the condensation of ketones with aldehydes in presence of ammonia, and on his use of caustic potash as a condensing agent. The careful investigation of a large number of such condensation reactions and the elucidation of the constitution of the compounds produced in these reactions or prepared as derivatives therefrom, not only formed a very important and valuable contribution to synthetic organic chemistry, but also enabled Japp to elucidate the constitution of important compounds prepared by other investigators. Thus, by condensing benzil with benzaldehyde in presence of ammonia, lophine was obtained, and the constitution of this compound, first prepared by Laurent and by Fownes, was thus

shown to be 
$$\begin{array}{c} C_6H_5 \cdot C \cdot NH \\ | \\ C_6H_5 \cdot C \cdot N \end{array} > C \cdot C_6H_5.$$
 By the reduction of lophine, amarine, 
$$\begin{array}{c} C_6H_5 \cdot C \cdot NH \\ | \\ C_6H_5 \cdot C \cdot NH \end{array} > CH \cdot C_6H_5,$$
 is formed (J., 1882, 41, 323; 1900, 77, 608).

Further, condensation of benzoin with benzonitrile under the influence of concentrated sulphuric acid showed that Laurent's benzilam (Zinin's azobenzil) is triphenyloxazole; and the oxidation of anhydracetonebenzil to desyleneacetic acid and the reduction of this acid to  $\beta\gamma$ -diphenylbutyric acid, which was found to be identical with Zinin's pyroamaric acid, established the constitution of the latter. By other condensations, also, important light was thrown on the constitution of glyoxaline, 
$$\begin{array}{c} CH \cdot NH \\ | \\ CH - N \end{array} > CH,$$

glycosine,  $\begin{array}{c} \text{CH}\cdot\text{NH} \\ | \quad \diagup \\ \text{CH}-\text{N} \end{array} > \text{C}=\text{C} < \begin{array}{c} \text{NH}\cdot\text{CH} \\ | \quad \diagdown \\ \text{N}-\text{CH} \end{array}$ , and lepiden (tetraphenylfurfuran).

Whilst the scientific investigations to which reference has just been made established Japp's reputation as a chemist of the first rank, the address which he delivered as President of the Chemistry Section of the British Association in 1898 made a wider appeal, and showed that he was not a mere specialist with his interests confined within the bounds of his own narrow branch of work, but that he interested himself also in the more fundamental problems of science and of life.

In that address, Japp emphasised the importance of the discoveries in stereochemistry because they furnish a reply "to the most fundamental question that physiology can propose to itself—namely, whether the phenomena of life are wholly explicable in terms of chemistry and physics; . . . or whether, on the contrary, there are certain residual phenomena, inexplicable by such means, pointing to the existence of a directive force which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms, determines the course of their operation within the living organism." His whole address was an argument, based on the results of stereochemical investigation, in favour of the doctrine of vitalism as revived by the younger physiologists; and in it his purpose was to show that "living matter is constantly performing a certain geometrical feat which dead matter, unless, indeed, it happens to belong to a particular class of products of the living organism and to be thus ultimately referable to living matter, is incapable—not even conceivably capable—of performing."

The argument may be briefly summarised. Although in nature most asymmetric compounds occur in one of the optically active forms only, it is found that when it is attempted to synthesise such a compound from symmetric substances the product of the synthesis is always inactive. As Pasteur said: "Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life and all others." The inactive forms, however, obtained by chemical synthesis can be resolved into the two oppositely active isomerides by means of enzymes, moulds, etc., and even, in some cases, by crystallisation. Since the racemic sodium ammonium tartrate could be resolved into the active forms by the symmetrically acting process of crystallisation, and these active forms could be separated by hand, it was thought that "the barrier which M. Pasteur had placed between natural

and artificial products" was thereby broken down; and this was undoubtedly the view held by the majority of chemists.

But had it? Japp intimated in his address that he had for some time held a contrary opinion, and he again asked the question which had also previously been posed by Crum Brown: "Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum*?" This question Japp discussed and answered in the affirmative. The artificial, racemic compound, certainly, had been resolved into the active forms by the symmetrical process of crystallisation, but these two forms had not thereby been *separated* from each other; both active forms were present side by side. Their separation "requires the living operator, whose intellect embraces the conception of opposite forms of symmetry, to separate them." . . . "Conscious selection here produces the same result as the unconscious selection exercised by the micro-organism, the enzyme, or the previously existing asymmetric compound." Pasteur had himself pointed out that "to transform one inactive compound into another inactive compound which has the power of resolving itself simultaneously into a right-handed compound and its opposite, is in no way comparable with the possibility of transforming an inactive compound into a *single active* compound. This is what no one has ever done; it is, on the other hand, what living nature is doing unceasingly before our eyes." Here then is the conclusion to which, from a consideration of the facts of stereochemistry, Japp arrived: "The production of single asymmetric compounds, or their isolation from the mixture of their enantiomorphs, is the prerogative of life. Only the living organism with its asymmetric tissues, or the asymmetric products of the living organism, or the living intelligence with its conception of asymmetry, can produce this result." And further: "I see no escape from the conclusion that, at the moment when life first arose, a directive force came into play—a force of precisely the same character as that which enables the intelligent operator, by the exercise of his will, to select one crystallised enantiomorph and reject its asymmetric opposite." The action of such a directive force, moreover, involves no violation of the law of the conservation of energy.

An address on such a subject as that selected by Japp could not fail to provoke discussion, and its arguments were, indeed, assailed by Karl Pearson, Fitzgerald, Herbert Spencer, and others. All their criticism, however, was successfully met, and failed to force a retreat from any of the positions which had been taken up.



That the work which Japp accomplished for chemistry was appreciated by the scientific and academic world is shown by the honours of which he was made the recipient. As early as 1885, he was elected a Fellow of the Royal Society; from 1885 to 1891, he was Foreign Secretary, and from 1895 to 1899, Vice-President of the Chemical Society; in 1891, he was awarded the Longstaff Medal, the highest mark of appreciation which British chemists can show, for his researches in organic chemistry; in 1898, he was President of the Chemistry Section of the British Association; and from 1901 to 1904, he was Vice-President of the Institute of Chemistry. In 1888, the University of St. Andrews conferred on Japp the Honorary Degree of LL.D., and he was similarly laureated by the University of Aberdeen in 1915.

A sketch of Japp's scientific achievements, however, gives a picture of but half the man; for in him we find one who, although a specialist who won for himself high distinction in a relatively narrow field of scientific study, nevertheless appreciated and loved literature and art. A linguist of ability, the literatures of England, Germany, France, and Italy were accessible to him in the language of their authors; and while possessing a familiar knowledge of all that is best in the literature of our own country, his acquaintance with the literature of Germany, of France, and of Italy was such as might be envied by many who have taken up the study, not of science, but of letters. On many occasions an apt quotation or literary allusion gave point to an argument or brightened a conversation.

In his speech, as in his writing, Japp's language was always clear and accurate, and if he did not compose with rapidity he did so with exceeding care; and his writings were models of lucidity, logical development of an argument, and accuracy of expression.

Japp's interests extended, also, into the realm of Art, especially of music. A musician of cultivated taste, he possessed not only executive ability as a pianist but also a thorough knowledge of musical theory and a wide acquaintance with musical compositions. It was to him a great pleasure, relaxation, and recreation to spend an evening, in the company of music-loving friends, in discussing the compositions of his favourite composers or in performing their works.

Unskilled in the art of self-advertisement and indifferent to the world's estimates of eminence or wisdom, Japp looked upon the general activities of the world and the impatient hurrying of men with a certain Olympian detachment and philosophic calm; and the petty annoyances which were laid upon him by the jealousies or inconsiderateness of lesser minds he bore with amiable

resignation. He was slow to form conclusions, but his judgment, whether of men or of opinions, was sound and could be relied on with confidence. He was himself the soul of honour and devoted to truth.

A product of the old *régime* in Arts in the Scottish Universities which, whatever its defects, cultivated width of view and diversity of outlook, Japp looked out on life through many windows, and to know him was in itself a liberal education.

In 1914, Japp retired from the Chair of Chemistry at Aberdeen and resided at first at Acton and later at Richmond, where he died. The closing years of his life were saddened by the loss of his son, who died, in 1920, while on the threshold of a promising career, from an illness contracted while on military service. In 1921, Japp's health broke down and he had to undergo an operation from which he never fully recovered; and in his last years, failure of eyesight deprived him of the companionship of books.

In 1879, Japp was married to Elizabeth Tegetmeyer, of Kelbra-Kyffhäuser, a small town near Nordhausen, by whom together with two daughters he is survived.

A. F.

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### FRANCIS JONES.

BORN 1845; DIED OCTOBER 22ND, 1925.

FRANCIS JONES was born in Edinburgh in 1845 and was educated at the Edinburgh Institute and the University. He went to Heidelberg to work under Bunsen, and here he met Roscoe. On returning to England he became one of Roscoe's two assistants in the great work on the atomic weight of vanadium. For Roscoe he always expressed great admiration, but it was a disappointment to him that no acknowledgment of his help appeared in the great paper. He used to say, with a whimsical smile: "I was only referred to as Analyst A or Analyst B, I forget which." On the retirement of Dr. Marshall Watts, Jones was appointed chemistry master at the Manchester Grammar School. The High Master was then F. W. Walker, one of the few non-clerical headmasters at the time. Realising, as few of his confrères did, the possibilities of science as a means of education, he gave Jones a free hand, and success came at once. Scholarships at the older universities were offered for science, and Manchester secured a very large number. In 1879, no fewer than thirteen of these coveted distinctions were won by Manchester boys, probably a record for the science side of any school. There was no extra preparation for scholarship boys, either in physics or in chemistry. Both Jones and

John Angel, the physics master, believed in letting boys teach themselves and each other, and, beyond the formal lectures and a little instruction in the chemical laboratory, the masters left the boys to work out their own salvation. To a modern schoolmaster, the liberty allowed to the Science Sixth would seem incredible. Many an afternoon would be spent in the Manchester Free Library, or in the ever-delightful quietude of the fifteenth-century library of the Chetham Hospital near by.

Besides Jones's personality, what affected us boys most was seeing him always at work on research. Many of those who have since given their lives to original investigation, owe most of the impetus which has driven them on, to the work on boron hydride which they watched in progress. The complete destruction of a large charcoal stove in which boron trioxide was being heated with magnesium, and the carrying off of R. L. Taylor, Jones's collaborator, to the infirmary, were incidents which made an impression never to be effaced on those of us who saw it.

In the new laboratory at the top of the main block of buildings, Jones had at last a place worthy of himself. His special pride was a very large and well-ventilated draught cupboard. In this the writer attempted, in its first week, the isolation of the still unknown oxide of bromine. About 15 c.c. of liquid monoxide of chlorine were mixed with a quantity of dried silver bromide, and not only was all the frame work and glass shattered to pieces, but the 3-inch slate bed was broken. All Jones said, when he contemplated the wreckage, was: "Well, it was what it was made for."

He died, at the age of 80, on October 22nd, 1925. His memory will always be cherished by his old pupils, who were also his friends. No schoolmaster had an influence like his on the making of a chemist.

H. B. B.

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### EDMUND KNECHT.

BORN JANUARY 29TH, 1861; DIED DECEMBER 8TH, 1925.

EDMUND KNECHT was born in Liverpool. His father, Gustav Knecht, B.Sc. (London), was a man of exceptional gifts as a schoolmaster, and his mother a Lancashire woman of singular charm. When Edmund was ten years old, the family settled in Southport, where his father conducted a school with much success for several years. From here the family, consisting now of three daughters and two sons, moved to the neighbourhood of Zurich, where a residential school was started on a largish estate. But the responsibilities and worries attendant thereon were too heavy and the

Knechts finally moved into Zurich itself. Edmund by this time was of an age to enter the University. He had natural leanings towards engineering, in fact his manipulative and mechanical skill was very marked. It was, however, his quick perception and interest in chemistry which attracted the notice of Victor Meyer, then Professor at Zurich University, and he induced Knecht to take up the study of this branch of science. At the age of twenty-one Knecht secured his Ph.D., his thesis being concerned with the homologues of resorcinol, and ultimately he became assistant to Victor Meyer. At this time Knecht saw a good deal of Sandmeyer, and the two remained all their lives the closest of friends.

Knecht soon after (1883) was offered the post of Head of the Chemistry and Dyeing Department of the Bradford Technical School which he occupied until, in 1890, there came a call to the Manchester College of Technology, in which institution he was actively engaged for the remainder of his life, as Professor of Tinctorial and Technological Chemistry, or as Associate Professor of Applied Chemistry of the University of Manchester. During a considerable portion of these thirty-five years Knecht was hard at work most days, including three evenings a week as well as Saturday afternoons. His influence on the students was remarkable both in the laboratories and in the lecture room. Few men of his time had so great a gift of inspiring their students with enthusiasm for their subject. Not only at home, but throughout the world, there must be thousands who have had the benefit of his tuition and his influence, and who regarded him with the utmost esteem both as a teacher and for his genial human qualities. His interest in his students did not stop with the conclusion of their academic career. He was wonderfully successful in finding them suitable posts, keeping track of them afterwards, and maintaining an interest in their future. Many are the chemists who would not hesitate to ascribe largely to Knecht's influence whatever success they have attained.

When the Society of Dyers and Colourists was formed in 1884, Knecht was appointed Editor of the Journal (1884—1893), which position he afterwards shared first with C. Rawson (1893—1899) and later with Professor W. M. Gardner (1899—1925). A large number of members assembled last year to commemorate the fortieth year of Professor Knecht's editorship and to make a handsome presentation to him subscribed to by his admirers, resident in all parts of the world.

The editing of the monthly journal just referred to claimed Knecht's close attention, but despite this he published in 1889 in conjunction with Benedict, "Chemistry of Coal Tar Colours," then

in conjunction with Christopher Rawson and Dr. R. Lowenthal that very widely-known text-book, "A Manual of Dyeing," unique of its kind; another treatise, "The Principles and Practice of Textile Printing," was published in conjunction with J. B. Fothergill. Yet another publication is entitled, "New Reduction Methods in Volumetric Analysis," by himself and Eva Hibbert. Many of the new analytical methods described in this volume have been widely adopted in chemical works at home and abroad. The methods are specially applicable to the rapid volumetric estimation of a great variety of substances including iron, sugar, and many dyestuffs. Two editions of all these books have been printed. Knecht was a contributor of many articles to the "Encyclopædia Britannica" as well as to Thorpe's "Dictionary of Chemistry."

Knecht's original research work is recorded in some 120 papers in the *Journals* of the Society of Dyers and Colourists, the Chemical Society, and the Society of Chemical Industry, the *Berichte*, and elsewhere. An enumeration of the titles of all of them appeared in the first-mentioned journal in June, 1925, and February, 1926. His contributions to our knowledge of chemistry range over an extraordinarily wide field. Many are closely connected with industrial, others again with pure chemistry. The major part of his researches was in relation to the chemistry of dyes, to the theory of dyeing, and to the application and manufacture of dyes. But as a glance at the titles of his many papers will show, he gave particularly close attention to all matters connected with the chemical and physical properties of textile fibres, especially cellulose and its derivatives, and he published interesting researches on the constitution of soot, and French and American rosin.

Knecht's system of volumetric analysis by the use of titanous salts, originally only intended to be applicable to the estimation of organic dyestuffs, has been so widely extended as to cover analysis of a great variety of other organic, as well as inorganic, substances. The extraordinarily wide applicability of these methods of volumetric analysis are regarded by some as being of such great importance as even to overshadow his brilliant work on dyeing and the chemistry of cellulose.

Knecht's memory was prodigious and, having read widely, he kept himself well up to date in all that touched upon the chemistry of dyes and of dyeing and of textiles. In these domains he was a perfect walking encyclopædia and could refer one, with unflinching trustworthiness, to almost any source of information upon which one desired enlightenment.

Knecht's modesty was characteristic of so many truly great men; his heart was absolutely in his work, with little or no thought of personal advancement or financial benefit to himself.

The circle of his friends and admirers was a very wide one, although he was not much given to indiscriminate social activities. Probably he felt these might interfere too much with his always strenuous work.

As years advanced, Knecht's zeal and enthusiasm for his research work seemed to grow keener and more intense. This was true up to within a few weeks of his death. He then underwent two serious operations. From the effects of these he had not quite recovered when in December, after two months spent in Switzerland, he returned home in very trying weather conditions, as a result of which he quickly succumbed to an attack of bronchitis and, his heart being unable to withstand the further strain, he breathed his last at Marple in the county of Cheshire, where he had made his home for so many years.

I can say without hesitation that I have rarely come across a man who so well deserved the esteem and affection and gratitude of a great body of chemists. A host of them owe to Edmund Knecht that sound basis of scientific thought and enthusiasm for their subject without which so little can be accomplished that is truly worth while in the domain of chemistry. He did his best in his own special sphere of activities and none will deny that his best was very good.

ALFRED RÉE.

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### WILLIAM ROBERT LANG.

BORN 1870; DIED NOVEMBER 20TH, 1925.

THE late William Robert Lang was a graduate of the University of Glasgow (B.Sc. 1890, D.Sc. 1899) and resigned the lectureship in Organic Chemistry there to become Professor of Chemistry in the University of Toronto. He was a Fellow of the Chemical Society (1897) and a member of the Institute of Chemistry and was elected Fellow of the Royal Society of Canada in 1911.

One of Dr. Lang's first activities in Canada was the promotion of a Canadian Section of the Society of Chemical Industry, of which he was the first Chairman. His scientific interests lay chiefly in the application of chemistry to industrial problems, and his monograph on the chemical industries of the Dominion (*Trans. Can. Inst.*, 1905) formed the basis of the "Directory" published by the Canadian Government in 1921. Many other papers in the chemical journals bear his name, or the names of his students.

From 1889 until the day of his death, Dr. Lang was actively connected with the forces of the King. In Glasgow, his birthplace (1870), he served with the Lanarkshire Royal Engineers (Volunteers); the year of his arrival in Canada he was gazetted to the Second Field Company Canadian Engineers, which he commanded as Major (1902) and Lieutenant-Colonel (1912); at the coronation of King George V in 1911 he commanded the Canadian Infantry there present. On the outbreak of war in 1914 he was appointed to the Canadian General Staff, assumed the duties of Officer in Charge of military instruction for Military District No. 2, and became O.C. the University of Toronto contingent of the C.O.T.C. In 1917 he was gazetted Colonel, and in the following year was G.S.O. (1) Coast Defence in the Maritime Provinces at Halifax N.S.

At the close of the war, Colonel Lang resumed command of the reorganized C.O.T.C. contingent, and resigned the professorship of Chemistry to direct the Department of Military Studies newly established in the University of Toronto; to the excellence of his work in this capacity high tribute was paid by Major-General MacBrien, Chief of Staff of the Canadian Militia, and a very keen critic, when at last year's inspection he said: "This is the largest O.T.C. inspection I have ever seen—and also the best."

Dr. Lang died very suddenly on November 20th last; the military funeral was preceded by a service at the University.

W. LASH MILLER.

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### FRANK GEORGE POPE.

BORN NOVEMBER 13TH, 1867; DIED OCTOBER 29TH, 1925.

FRANK GEORGE POPE was born on November 13th, 1867, the son of George Campion Pope and Teresa Pope. He received his early education at Haberdashers' School and afterwards proceeded to Finsbury Technical College with the intention of becoming an engineer. This intention was not realised, as he went to the Peoples' Palace Technical Schools as a demonstrator in the Chemical Department. At that time, East London College had not been thought of, and it was necessary to deal, not with matriculated students working for a degree, but with boys of 12 to 15 years of age belonging to a large day school and to spend four nights a week on evening classes, principally attended by junior works chemists and elementary teachers. Luckily, no classes were held on Saturdays.

When I first met Pope one evening in February, 1894, he was running a practical class of the stamp usual in those days and

trying to do some research in the store-room, as he had no private bench of his own at which he could work. The next month we joined forces and started a firm friendship which only ceased with his lamented death last October. Had it not been for his help, kindness, and extreme loyalty, my earlier days at the People's Palace would have been very different. Pope could manage boys; not being used to them, I could not. His methods were summary but just, and many an old boy must remember the penalties exacted for not taking down notes properly during lecture. Whilst boys had to work hard and keep the peace when in class, once the week's work was done, Pope would play cricket with them on Saturdays and for years attended the annual camp of Day School boys on the South Coast.

Pope very soon joined in some work that was interesting me; this was kept going at odd times between classes and, on Saturdays, we often met about 2 p.m. and went on until 10. Our earliest joint publications were concerned with fluorones, the "abnormal hydrates" formed by hydroxyazo-compounds and one or two new hydrazines. The fluorones especially interested Pope and he returned to their study in later years, his work (partly with H. H. Howard) and that of Kehrman clearing up many doubtful points.

In the later 'nineties, the nucleus of East London Technical College was formed with a number of day boys who had finished their three or four years' course and could be put on to more advanced work; in this way, a supply of research assistants was at last assured. Meanwhile, Principal Hatton was striving for the establishment of an East London College. Such a college has now been a school of the University of London for some years past.

A good knowledge of organic chemistry and great interest in the subject, together with a genial disposition, made Pope an excellent teacher. After an advanced organic lecture, he would come with the class into the laboratory, walk to a blackboard, start asking questions, expound views, and make the students show what they did or did not know.

From 1915, until the chair of chemistry was filled by the appointment of Professor Partington, Pope acted as head of the Chemical Department, and the College authorities made him an Assistant-Professor. He had been a Reader in the University for some years. The burden during the war was considerable and the subsequent work heavy, as East London College, like other institutions, suffered from a surfeit of students.

During a well-earned holiday in 1922, peritonitis supervened on food poisoning and after an operation in Switzerland it was some months before Pope returned to England. For a time, he con-



tinued his work at East London College, but it was evident that his health was broken and he had to retire in 1923. His old students and colleagues made him a presentation at the Old Students' Association dinner in January, 1925. This was the last College function he attended. After further months of illness, he died on October 29th, 1925.

Pope was beloved by his pupils and colleagues. Students who shirked or exhibited too much conceit had reason to regret their faults, but anyone who desired aid found in him a ready helper. Like many other chemists, he enjoyed out-door life and it was a delight to sit with him on a Surrey hill, not bothering about the time of lunch or the return train to London.

He married Adelaide, daughter of Harold Field Downer. She and a married daughter survive him to mourn his loss. His old students and former colleagues remember a very unselfish friend to whom they owed many a debt for uniform kindness and consideration. No one realises this more fully, or holds his memory in deeper affection, than the present writer.

J. T. HEWITT.

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### CHARLES ETTY POTTER.

BORN JANUARY 5TH, 1880 : DIED SEPTEMBER 13TH, 1925.

CHARLES ETTY POTTER was born on January 5th, 1880, at Melsonby, near Darlington, at which place his father was headmaster of the Wesleyan school. An early aptitude for school work enabled him to gain a Flounder's scholarship with which he entered the North Eastern County School at Barnard Castle, and a successful school career was terminated by the winning of a North Riding scholarship tenable at the Yorkshire College. In his studies at Leeds, Potter's attention was directed to the physical sciences, and after graduating as B.Sc. of Victoria University in 1900, he pursued a post-graduate course in applied chemistry under Professor H. R. Procter in the leather industries department. In the development of various social activities at the Yorkshire College, Potter took a very active part, and the students' scientific, debating, and other societies were indebted in no small measure to his energy, enthusiasm, and determination.

On leaving the Yorkshire College in 1901, Potter accepted a post on the research staff of the Wellcome chemical research laboratories, where, for some years, in collaboration with Dr. F. B. Power and Dr. H. A. D. Jowett, he was engaged in the investigation of problems connected for the most part with complex organic compounds. Three papers published in the *Journal* of

the Chemical Society conjointly with H. A. D. Jowett, namely: "Preparation and Properties of 1:4(or 1:5)-Dimethylglyoxaline and 1:3-Dimethylpyrazole" (J., 1903, **83**, 464), "The Constitution of Chrysophanic Acid and of Emodin" (*ibid.*, p. 1327), "The Constitution of Barbaloin" (J., 1905, **87**, 878), indicate the nature of the work on which he was engaged. The *Pharmaceutical Journal* affords a record of other work with which Potter was associated during this period.

In January, 1906, Potter was transferred to a position in the analytical department at the Dartford works of Messrs. Burroughs Wellcome and Co., but towards the end of the same year he decided to take up teaching work. For a short time he was engaged at the Abergele Council school, but his chief teaching work was done at the Heckmondwike Secondary school where for 10 years he was engaged in teaching chemistry, physics, and mathematics and was responsible for the organisation of courses of instruction in physical science adapted to the requirements of a scheme of home training for girl pupils. For the greater part of this period he was also in charge of evening chemistry classes at the Batley Technical College. Early in 1916, he obtained an appointment as research chemist with Messrs. Levinstein, Ltd., at Blackley, Manchester, which position he retained after the amalgamation of Messrs. Levinstein with British Dyes, Ltd., and at the time of his death he was in the service of the British Dyestuffs Corporation, Ltd. As a member of the staff of the technical research department in this concern Potter was not only associated with the laboratory research work on colouring matters, but with problems incidental to large-scale production; he also held a position of considerable responsibility in connexion with the engagement and welfare of chemical assistants in the technical departments. He took a keen interest in the activities of the Manchester sections of the Society of Chemical Industry and the Institute of Chemistry, and served on the Committee of the latter for a period of three years.

Many of his Yorkshire friends had an opportunity of meeting him at the annual meeting of the Society of Chemical Industry at Leeds in July, 1925. Those who took part in the excursion to Huddersfield were particularly impressed by the lively and illuminating manner in which Potter explained certain of the processes carried on in the works of the British Dyestuffs Corporation. Towards the end of the same month he became seriously ill as the result of an insect bite on the scalp, and, in spite of every attention, died in the Manchester Royal Infirmary on the 13th September, and was buried in the grounds of St. Margaret's church at Prestwich on September 16th. He left a widow and three sons of school age.

For information relating to Potter in the period subsequent to his University studies, the writer is much indebted to Mr. F. H. Lees, the Head of the analytical department of Messrs. Burroughs Wellcome and Co. Potter is described by him as an enthusiastic worker, exhibiting unusual initiative and resourcefulness in overcoming the difficulties inseparable from original research. His cheerful disposition never deserted him under the most trying conditions and his relations with his colleagues were of the most cordial kind. He always strove to uphold the traditions of his Alma Mater and often became eloquent in insisting upon how much he was indebted to his chemical teachers at Leeds. The characteristics portrayed in this description would appear to have been retained in undiminished measure in the later period of his life, and his fellow chemists deplore the loss of a colleague whose integrity and sincerity were universally acclaimed.

H. M. DAWSON.

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#### ROBERT LLEWELLYN TAYLOR.

BORN NOVEMBER 21ST, 1851; DIED NOVEMBER 8TH, 1925.

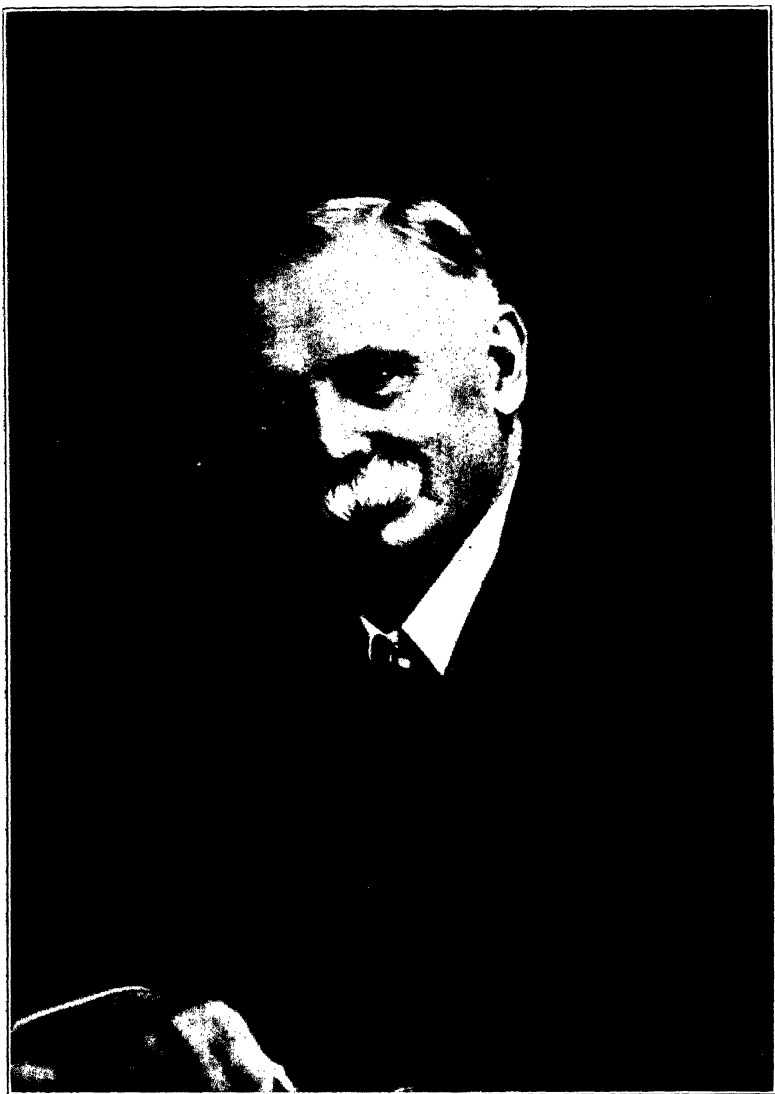
ONE of the pioneers of the teaching of science in this country and a man of high scientific attainments, R. L. Taylor passed away at his home in Whalley Range, Manchester, after a sudden heart attack. He will be sadly missed by many friends and associates, who welcomed a meeting with Taylor as one of their real pleasures. Always enthusiastic in the pursuit of chemical knowledge, of a cheery and kindly disposition, he carried a warm atmosphere about with him.

Taylor was born at Sabden in the Pendle Hill district and as a boy he attended the village school there. At fourteen years of age, he was employed at the print works at Sabden, of which his father was the manager. His parents originally intended that he should learn the business of a calico printer and during four years he spent the daytime in this way. In the evenings he studied the science of chemistry and fitted up a disused room in the works as a chemical laboratory. The course which he followed was no easy one, for he had no teacher, but it was at the same time a fine training ground, because it enabled him to understand the difficulties of others when in later years he became a teacher. After his four years' work at Sabden, he was appointed lecturer's assistant to Dr. A. W. Williamson, Professor of Chemistry at University College, London. Here Taylor made the most of the fine opportunity which presented itself of acquiring skill in experimental and research work. In 1872 he was appointed assistant master in the

chemical laboratory of the Manchester Grammar School and in this position his teaching ability soon made itself manifest. Taylor was associated with Mr. Francis Jones at the Grammar School in the discovery and investigation of boron hydride and the work was published in the *Journal* of the Chemical Society. In 1878, Taylor became teacher of chemistry and physics under the School Board and later he became organising master and inspector of science classes to the Manchester Education Committee. The work from 1880 to the date of his retirement under the superannuation act in 1919 involved both day and evening class duties. In spite of this, he managed to find time for many original investigations and his pupils could realise that they were receiving not merely book lore, but first-hand knowledge from one who worked for the love of science. His research was not made easy by the possession of a well-equipped chemical laboratory and he was always grateful for the encouragement of friends and for the assistance afforded by the loan of some simple piece of apparatus. The records of some of his work appear in the *Transactions* of the Chemical Society, in the *Journal* of the Society of Dyers and Colourists, and in the *Memoirs* of the Manchester Literary and Philosophical Society. They embrace a very exhaustive study of bleaching powder and its action in bleaching, the action of bleaching powder on various natural colouring matters, the effect of light on solutions of bleaching powder, a comparison of the bleaching action of hypochlorous acid and chlorine, and a method for the determination of chloric acid and chlorates. In 1911 he was awarded the research medal of the Worshipful Company of Dyers. In earlier years, Taylor introduced a method for the separation of cobalt and nickel and carried out work on a higher oxide of cobalt and on white ferrous ferrocyanide. His chemical text-books are widely known and include "Analytical Tables for Chemical Students," "Chemistry for Beginners," "The Student's Chemistry," and "Chemistry for Evening Continuation Schools." In 1922 Taylor issued and edited a small book, entitled "Bleaching Powder and its Action in Bleaching," embodying his original memoirs on the subject of bleaching powder.

Many distinguished scholars owe their first inspiration to the teaching and guidance of Taylor. In addition to his scientific attainments, he was able in his leisure hours to provide entertainment for old and young by his lectures and demonstrations such as those on soap bubbles and methods of obtaining a light. With a lively party of boys he would explore the wonders of Castleton, the beauties of Ingleton, and the mysteries of Whalley. His interest in the subject of sound extended still further his love of





Yrs very truly  
F. S. Thompson

music and he conducted an orchestra in the Central High School in Manchester.

There is a vacant place in the Manchester Literary and Philosophical Society, of which he was a member of the Council. He was a member of the Chemical Society from January 1874 until the date of his death.

[The late] EDMUND KNECHT.

### SIR EDWARD THORPE.

BORN DECEMBER 8TH, 1845; DIED FEBRUARY 23RD, 1925.

IN the death of Sir Edward Thorpe, which took place at Whinfield, his residence at Salcombe, South Devon, on February 23rd, 1925, in his eightieth year, the Chemical Society lost a former President, whose membership extended over 54 years, and who during this period served the Society as Member of Council, Vice-President, and Treasurer for ten years, from 1899—1909. The record of Sir Edward Thorpe's activities and achievements in chemistry is a full and varied one. Successively he filled with distinction and success the Chair of Chemistry in three institutions. He was appointed to the Andersonian College, Glasgow, in 1870, having as forerunners Birkbeck, Gregory, and Graham, "an honourable and distinguished ancestry," of which he was justly proud. Then in 1874 Thorpe was appointed Professor of Chemistry in the newly-founded College at Leeds, the Yorkshire College of Science, as it was at first styled, the second of those provincial colleges which owed, in no small measure, their formation to the stimulus which the success of Owens College, Manchester, had given to the movement for the provision of university education in the provinces. This appointment must have appealed especially to Thorpe, himself a first and one of the best products of the provincial university college, affording, as it did, opportunities of putting into practice the system of educative work of which he had had experience in the years spent at Owens College. At that time (1873) Owens College had just emerged from its temporary housing to occupy the first block of buildings on the present site of the University of Manchester. Thorpe was fortunate in having as colleagues men so distinguished as Green, Miall, and Rücker, with whom he laid the foundation and traditions of an institution from which the University of Leeds has grown. When in 1885 Thorpe resigned the post at Leeds to become the successor of Sir Edward Frankland at the Royal College of Science in London, he had the satisfaction of seeing the Yorkshire College housed in new and appropriate buildings, with well-designed and equipped chemical

laboratories and lecture theatres. In the year 1894 he was appointed the Director of the Government Laboratories and was responsible for their design and equipment. Shortly before his retirement, in 1909, he accepted the invitation to resume the Professorship of General Chemistry at the Imperial College of Science and Technology, which had been formed by the amalgamation of the Royal College of Science and the City and Guilds Institute at South Kensington. This position he finally resigned in 1912.

The discharge of the duties of these various positions, and the demands made on his time and energy in the building up of a new college at Leeds, did not prevent Thorpe from maintaining a steady output of scientific investigations and research. Furthermore, throughout his life, he maintained a literary activity; the volume of collected essays on Historical Chemistry, the memorial lectures on Kopp, Victor Meyer, Cleve, and Thomson, as also the articles on scientific worthies contributed to *Nature*, constitute examples of the highly valuable additions made to chemical literature and afford illustrations of the clearness in style and the extensive knowledge which characterised his writings. Thorpe's interest in the history of chemistry is shown by the selection of subjects for addresses. At the Leeds Meeting of the British Association in 1890, Priestley, Cavendish, Lavoisier, and *La Révolution Chimique* formed the subject of the address delivered to Section B (Chemistry) on that occasion; and again, ten years later, he selected for the Presidential Address to this society "The Progress of Chemistry in Great Britain and Ireland during the Nineteenth Century." Further, among other valued contributions to chemical literature are the biographies of Priestley, Davy, and of his teacher, Roscoe.

In more prosaic fields, mention should be made of his text-book of Inorganic Chemistry, published in two volumes, the text-books of quantitative and qualitative analysis, and of the monumental work, "The Dictionary of Applied Chemistry," the preparation of a new and enlarged edition of which occupied him to within a few weeks of his death.

Thomas Edward Thorpe, the son of George Thorpe, a Manchester merchant engaged in the cotton trade, was born on December 8th, 1845, at Barnes Green, Harpurhey, near Manchester. His early education he received at the Manchester Diocesan School (Hulme Grammar School), and in 1863 he entered Owens College as a student in the Chemical Department under Professor Roscoe. Here he remained for four years, acting for the greater part of this period as private assistant to Roscoe, taking an active part in the photochemical researches, the investigation of perchlorates, and in the classical work on vanadium, which ultimately resulted in



assigning to this element its true position in the classification of the elements. In the obituary notice of Sir Henry Roscoe, Thorpe has given an account of much of the work of this period, and in connection with the vanadium investigation he wrote: "It was the writer's privilege to assist in the early stages of this investigation, and it fell to his duty to carry out the various experiments which eventually served to establish the composition of the oxides of vanadium, the true nature of its volatile chlorides, the existence of hitherto unknown oxychlorides, and of the mononitride which Berzelius regarded as the metal, and lastly to fix its real atomic weight and to show that it was apparently 16 units below that assumed by Berzelius on the mistaken supposition that vanadium compounds were analogous in composition to those of chromium."

In connexion with the photochemical researches, Thorpe journeyed in 1866 to Pará on the Amazon, and in the autumn of 1867 he made a long series of observations under a cloudless sky at Moita, near Lisbon, concerned with the relation between the sun's altitude and the chemical intensity of daylight. It was on the return journey from Pará that he made a series of determinations of the carbon dioxide present in the air over the ocean, and succeeded in establishing a constancy in the daily and nightly proportion of 3 volumes of carbon dioxide per 10,000 volumes of air, thus confuting the conclusions drawn by Lewy, who maintained that the proportion of carbon dioxide in the air over the ocean exhibited a diurnal and nocturnal variation. In recognition of this work Thorpe was awarded the Dalton Scholarship in Chemistry.

Mr. J. Kentish Wright of Nottingham, a fellow student and life-long friend of Thorpe, has furnished the writer with the following recollections:

"I first came into intimate association with Thorpe (then universally known as Tom Thorpe) in the year 1865 when we were both students at Owens College, Manchester, and were elected joint Secretaries of the Students' Union. Previous to this I had only known him slightly, as he was entirely a 'science' student, and I was entirely an arts student; as far as I remember, we never attended the same lectures but were constantly meeting on union matters; we soon found we had many tastes and interests in common. He was widely read in modern literature and had a very keen appreciation of Dickens and Thackeray, and we had many talks as to our favourite novels. His distinguishing characteristic was his extraordinary vitality and energy, which he put into whatever he was occupied with, and which enabled him to excel in whatever he undertook. Of his eminence in science I was then and am now unable to judge, but the distinction he attained is sufficient

evidence of this. He was, moreover, a skilful writer of popular sketches and verses, which appeared in the Students' Magazine, and was the author of a very interesting account of the rubber gatherers of South America.

"He had a very strong sense of humour and love of fun, was an excellent story-teller, and could enjoy a joke against himself.

"He was an ardent sportsman and lover of athletics, and took a very active part in originating the boat races, which were rowed on the Irwell between the Science and Arts students. These were started in 1864 and continued for many years. He coxed and coached the Science boat, and on one occasion, although of small stature, he rowed bow in that boat.

"He was also a keen cricketer and a useful bat, playing regularly for the college eleven.

"About this time he introduced me to the young lady (Miss Emma Watts, daughter of Dr. John Watts) to whom at that early age he was engaged and to whom he was devoted the whole of his life. They were married in 1870, at the Manchester Cathedral, and I was present as one of his groomsmen. Lady Thorpe is now living at his beautiful home at Salcombe, South Devon.

"In later years his great pleasure was yachting, and he has written several books describing his cruises. It was soon after he went to Glasgow (about 1871 or 1872) that he bought a small cutter yacht and invited me to go with him on a cruise to the Hebrides. I was terribly disappointed that I could not accept, but subsequently I had reason to congratulate myself. Thorpe sailed the yacht up to Skye and anchored off the coast there—but the wind got up in the night—the anchors dragged and the boat was driven on the rocks and became a complete wreck. There was a small dingy and in this Thorpe and his brother-in-law, Harry Watts, and the two men forming the crew managed to reach the shore. If I had been there, in all probability the dingy would not have carried all and there would have been a tragedy. They spent the night shivering on the rocks, and in the morning found themselves in the most desolate part of Skye—eight miles from the nearest house.

"Although our paths diverged in after life, we kept up our friendship to the end of his life by correspondence and occasional visits. It was always an unfailing delight, when we met, to recall the old days and to tell over again the old stories and reminiscences. The last time I saw him was in the year 1921, when he stayed a few days with me on his road to Edinburgh for the British Association Meeting. Thorpe told me an amusing story about Lloyd George, whom, by the way, Thorpe much resembled in stature and

appearance, and for whom he was often mistaken. Lloyd George, when Chancellor of the Exchequer, wished to put a tax on petrol or other spirits used for motors, and sent for Thorpe, who was then Government Chemist, to obtain the proper word to comprise petrol, benzoline, paraffin, and anything else used for that purpose. Thorpe disapproved of the proposed tax, and determined not to help Lloyd George. He said, 'There is no one in England knows more about it than I do, and I can't find a word, and if I can't, no one can.' Lloyd George jumped up and ran to Thorpe and seized him by the lapels of his coat and shook him vigorously, saying, 'Look here, you can help me and you've got to help me—you can help me and you've got to help me.' Thorpe went away quite won over by Lloyd George's fascination and powers of persuasion. He spent a sleepless night pondering the problem, and with the dawn there flashed across his mind the phrase 'Motor Spirit,' which was accepted and has been in use ever since."

In *The Old Owensian Journal* for May, 1925, appeared an appreciation of Sir Edward Thorpe from the pen of the late Francis Jones, who wrote as follows :

"It was my good fortune to make the acquaintance of T. E. Thorpe in 1866 when I returned from Bunsen's laboratory in Heidelberg to become private assistant to Professor Roscoe in the Old Owens College in Quay Street.

"The Professor told me that he had obtained from the copper works at Alderley Edge a large quantity of a residue containing about 2% of vanadium, and he wished to make an investigation of the properties of that rare element and its compounds. He asked me to work at this along with T. E. Thorpe, who had been a senior student of the College, and I was soon after introduced to him. Thus began a lasting friendship between us, and for many months we worked together on what was to both a most fascinating research. We soon found out that what Berzelius considered metallic vanadium was really the lowest oxide, and this involved the lowering of its combining weight to 51.2. It was impossible to work in daily association with Thorpe without being attracted by his unfailing cheerfulness, genial humour and intimate knowledge of chemistry. The results obtained in the investigation were communicated by Roscoe in a paper read before the Royal Society. Our close association ended in 1867, when Thorpe went to Bunsen's laboratory, and soon after (1870) he became Professor of Chemistry in the Andersonian Institution in Glasgow, but we continued to meet from time to time and kept in touch with each other by correspondence.

"He helped me greatly in 1911 when I started a movement to

celebrate the centenary of Bunsen's birthday by sending an illuminated address and wreaths to the Pro-Rector of Heidelberg University, Professor von Duhn, who requested Bunsen's successor, Professor Theodor Curtius, to acknowledge the address and wreaths which were forwarded to Heidelberg in time for the celebration of the anniversary on March 31st, 1911.

"Professor Curtius wrote: 'The address will be framed and find its place in the Bunsen Room of the Chemical Institute with the picture and other mementos of the Master.' Thanks to Thorpe's help twenty-three former students of Bunsen's added their names to the address; these included Henry E. Roscoe, 1852—1855, Alex. Crum Brown, 1861—1862, W. Marshall Watts, 1865, Francis Jones, 1865—1866, T. E. Thorpe, 1867—1870, C. A. Burghardt, 1870, W. Carleton Williams, 1871—1872, J. Grossmann, 1872—1873, Arthur Schuster, 1872, Arthur Smithells, 1883, and G. H. Bailey, 1884—1885.

"I last saw Thorpe when he was President of the British Association in Edinburgh, when he was unfortunately unable, owing to illness, to be present at most of the meetings."

As has been already mentioned, Thorpe obtained the Dalton Scholarship in Chemistry and then proceeded to Heidelberg to study under Bunsen. The following is an extract from a letter published by Sir Henry Roscoe in his Autobiography from Thorpe in which he describes incidents of his arrival at Heidelberg and his reception by Bunsen:

"Well, in the autumn of '67 I set out for Germany, fortified with much good advice, and bearer of sundry presents from you and yours to Bunsen—among them a copy of *The Times* containing an account of a 'horrid murder' (you remember the dear old man's amiable weakness for 'horrid murders'), a small consignment—I think from Mrs. Roscoe, your mother—of potted shrimps (another amiable weakness), and above all some magnificent specimens of potassium and sodium (calculated to go straight to his heart) from Mather's works at Patricroft. Sonstadt had worked out Caron's process for the manufacture of magnesium, and there was what we then considered a great demand for the metals of the alkalis.

"After a leisurely journey up the Rhine—I remember seeing the white-coated Croats in garrison at Mayence—I found myself in Heidelberg and lost no time in presenting myself to Bunsen, armed with the copy of *The Times*, the potted shrimps, and the precious box containing the alkali metals. Although it was still vacation time, Bunsen had returned to work. I was ushered into the little room you know so well, overlooking the Wrede Platz. The great man—great physically as well as intellectually—rose from

the table at which he was writing—I see him now—and motioned me to the sofa. He evidently was not unprepared for my coming—I suppose you must have informed him. I duly presented your letter of introduction and, after answering his many tender inquiries concerning you, moved up my heavy battalions. I received a momentary check, however, for owing partly to his slight deafness but much more to my imperfect knowledge of German, he moved across to the sofa the better to hear me and sat down on my hat! I at once brought *The Times*, the potted shrimps, and the alkali metals into action. The ‘horrid murder’ he would read at bedtime: the potted shrimps would certainly be appreciated in the morning: and we prepared ourselves for the alkali metals. The servant was called to unpack the box, when to my consternation he produced a bottle—I remember it was an old pickle-bottle—partially filled with naphtha, at the bottom of which were a few tablespoonfuls of a bright shining rather mobile fluid. I had given the Geheimrath such a glowing account of the size of the sticks of the two metals that I was simply speechless with astonishment and felt indeed rather like an impostor. I had never realised so vividly before the possibility of the transmutation of metals. ‘Well,’ I said at last, ‘potassium and sodium were certainly put into the bottle before I left home, but what is there now is uncommonly like quicksilver.’ ‘No,’ said Bunsen, who was holding the bottle, ‘it is not quicksilver. Feel the weight of it!’ The fact was that our old friend Heywood, who had been ordered by you to pack the specimens at the time in separate bottles, perceiving that both could be got into one bottle, had, with the charitable idea of not encumbering me with too bulky a package, placed the two metals together, with the untoward result I have indicated. Chemical combination between solids is not of frequent occurrence, but that it is possible under certain circumstances has never been forgotten by me. I had no knowledge at the time of the existence of the fluid alloy—nor had Bunsen—which, perhaps, is not very creditable to us, since it is actually mentioned by Davy. As an historical fact, I believe the first so-called potassium isolated by Davy was fluid at ordinary temperatures owing to the amount of soda in the electrolysed potash.

“I assure you I felt a little limp at the moment—more limp, indeed, than my crushed hat—and, conversation flagging, he suggested that he should show me the place where he intended that I should work. It was in his own little laboratory, a couple of benches away from him, and where I had as companions Victor Meyer and an American—Gideon Moore—a man of extraordinary

ability, who had the misfortune to be stone-deaf, but who taught himself German and spoke it fluently without having heard a sound of the language."

Thorpe's memorial lectures on Kopp and Victor Meyer enable us to gather something of the impressions made by the life and work at Heidelberg. His fellow students included many whose names are writ large in chemical literature, *e.g.*, Erlenmeyer, Ladenburg, Horstmann, Ludwig, Cohen (the mineralogist), Rose, and Emmerling. Thorpe was undoubtedly greatly attracted to Kopp, whose influence and teaching are to be seen in his own researches on specific volumes and other physical constants, remarkable for their exactitude.

At Heidelberg he graduated as Ph.D., and during this period he published papers dealing with (1) nontronite, to which he assigned the formula  $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ , (2) the analysis of the ash of a diseased orange tree, and (3) observations on the physical properties of chromium oxychloride, directing attention to the identity in the molecular volumes of sulphuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) and chromium oxychloride ( $\text{CrO}_2\text{Cl}_2$ ). From the latter he obtained, by the action of heat, the solid oxychloride of chromium—chromium chlorochromate,  $\text{Cr}_3\text{O}_6\text{Cl}_2$ .

From Heidelberg Thorpe went to Bonn, and whilst there, worked with Kekulé on ethylbenzoic acid, which they isolated from the product of the action of carbon dioxide on sodium and an ethereal solution of ethylbromobenzene.

Returning to Manchester he joined, for what proved a short period, the teaching staff of the chemical department at Owens College, and in 1870 he was appointed Professor of Chemistry at the Andersonian College, Glasgow. Here the association with Young, the founder of the Scottish oil industry, led to the study of paraffin, and in conjunction they conducted a research on the action of heat and pressure on paraffin, which formed the subject of two papers. The authors noted but little gas to be produced, and from 4.5 kilograms of paraffin they obtained 4 litres of liquid hydrocarbons, which were separated into 2.7 litres boiling at 200—300°, 1 litre boiling at 100—200°, and 0.3 litre boiling below 100°. From this last fraction both amylene and hexylene were isolated.

Whilst at the Andersonian College Thorpe attempted, in the light of his experience with vanadium oxychloride, to prepare a lower oxychloride of phosphorus by submitting phosphorus oxychloride to the action of reducing agents, but found the phosphorus compound to behave quite differently, yielding phosphorus trichloride only, and giving no indication of the formation of oxychlorides similar to those of vanadium. The production of phos-

phoryl thioclauride by the interaction of phosphorus pentasulphide and carbon tetrachloride was noted. The determination of the solubility of silver chloride in concentrated nitric acid led to the conclusion that this solubility is of the order of 2 parts of silver chloride in 100,000 parts of concentrated nitric acid. During the tenure of the professorship at Glasgow Thorpe published the textbooks already referred to: (1) *Inorganic Chemistry*, in two volumes (Collins), (2) *Quantitative Analysis* (Longmans), and (3) *Qualitative Analysis*; in the production of this last M. M. Pattison Muir collaborated.

The translation to Leeds took place in 1874, when Thorpe was appointed Professor of Chemistry in the Yorkshire College of Science, with A. W. Rücker in the Professorship of Experimental Physics (with which was associated Mathematics) and A. H. Green in the Professorship of Geology and Mining. In the biography of Sir Henry E. Roscoe, Thorpe gives a sketch of the history of the foundation of the Yorkshire College, from which may be gathered some idea of the conditions under which a beginning was made. He writes:

"The premises in which the College was first housed consisted of a disused Bankruptcy Court situated in Cookridge Street, one of the main thoroughfares leading out of the town. After a somewhat chequered career, the building had been partially used as a school of cookery, with the unfortunate result that it had been largely consumed by a fire just prior to being taken over by the College authorities. Although not so spacious as Richard Cobden's old house in Quay Street, Manchester, in which Owens College first started, the Leeds building, in some respects, was not ill-adapted to the purposes of the limited professoriate with which the Yorkshire College of Science began its operations. At all events, it accommodated without the slightest difficulty all the students who sought admission to it on its opening day.

"The College began its work of teaching on October 26th, 1874—somewhat later than the normal opening of a session—owing to delays in completing the necessary structural arrangements. But as there was no yearning anxiety on the part of anybody to learn, no special inconvenience or disappointment resulted. There was no preliminary flourish of trumpets—hardly so much as an opening speech. The initial ceremony was as simple as the appointments of the College were modest. Each of the three professors in turn gave an introductory lecture to an audience consisting of members of the Council and such of the friends of the embryo institution as cared to attend. Some encouraging remarks were made by the Chairman, and so the College was launched. But for a time the

students were few and their advent as far between as the visits of angels."

Unless one has had the like experience, it is not easy to realise what the first years of such pioneering work meant and entailed. However, the work evidently progressed, as in 1877 the foundation stone of the new College buildings was laid, and before this the professoriate had been extended by the appointment of Professor L. C. Miall to the Chair of Biology, and later the establishment of Chairs of Classical Literature and History, and Modern Literature and History, to which Professor J. Marshall, M.A., of Balliol College, Oxford, and Professor F. S. Pulling, B.A. (Oxon), were, respectively, appointed. "This enlargement," Thorpe writes, "of the educational work of the College necessitated a slight but significant change in its designation: henceforward it became known as the Yorkshire College until it was raised to the rank of a university, when it took the name of the town in which it was situated."

The eleven years spent at Leeds were marked by a steady output of scientific work, and this despite the many and varied demands upon Thorpe's time and energy necessitated in establishing the new College. Amongst the researches of this period, researches marked by the accuracy characteristic of all Thorpe's work, are those concerned with the specific volumes of liquids. He was led to conclude from the specific volumes of phosphorus oxychloride and thiophosphorus chloride that in these compounds phosphorus functions as a tervalent element, thus giving support to the formula

$\begin{array}{c} \text{Cl} \\ \diagup \\ \text{Cl} \end{array} > \text{P} - \text{O} - \text{Cl}$  in preference to the formula  $\begin{array}{c} \text{Cl} \\ \diagup \\ \text{Cl} \end{array} > \text{P} = \text{O}$ , necessitating

a quinquivalent phosphorus. A few years later Thorpe was destined to provide evidence in support of the higher valency for phosphorus, by the discovery of the gaseous pentafluoride, as a product of the interaction of arsenic trifluoride and phosphorus pentachloride. The physical properties of this compound afforded a ready means of fixing its molecular weight, which with its analysis showed the molecular formula to be  $\text{PF}_5$ .

In a lecture to this Society, Thorpe, in 1880, gave an account of his work "On the relation between the molecular weights of substances and their specific gravities when in the liquid state." In recognition of the value of these researches he was awarded the first Longstaff Medal in 1881. Professor Roscoe, the President, in making this presentation, expressed himself as follows:

"Professor Thorpe: I consider it a special privilege that it falls to my lot to present to you, as one of my oldest and most distinguished pupils, the first Longstaff Medal awarded by the



Chemical Society for the best series of original investigations in chemistry published in England during the past three years, amongst which I may mention, as the most important, your discovery of phosphorus pentafluoride; that of the occurrence of heptane in *Pinus Sabiniana*, giving accurate determinations of its physical constants; and, last, the valuable contributions to Physical Chemistry in your researches on the relations between the molecular weights of substances and their specific gravities when in the liquid state. I trust that this recognition by the Chemical Society of your varied and successful labours will stimulate to further efforts, and that before long the Society may be benefited by other communications from your laboratory."

Amongst the communications from the laboratory of the Yorkshire College are to be found: "A Simple and Expeditious Method of Preparing Pyrogallol for Dry Plate Development"; "The Action of Zinc, Magnesium, and Iron as Reducing Agents with Acidulated Solutions of Ferric Sulphate"; "Note on the Action of the Oxychloride of Sulphur on Silver Nitrate"; "Contributions to the History of the Mineral Waters of Yorkshire"; and "On Dust Explosions in Collieries." Further, the re-determination of the atomic weight of titanium was made by Thorpe on the eve of his departure from Leeds. The memorable series of lectures delivered by Thorpe and his colleagues, under the auspices of the Gilchrist Trust, was published in 1878 and edited by him with the title "Coal, its History and Uses."

Considerable activity in research marked the nine years (1885—1894) of the Professorship at the Royal College of Science, as shown by the papers published, conjointly with others, during that period. The determination of the atomic weight of silicon, with J. W. Young, and of gold, with A. P. Laurie, gave the values 28.3 for the former and 196.7 for the latter of these elements. The investigation with Hambly of the vapour density of hydrofluoric acid, proved the density gradually to diminish between the temperatures of 26° and 88°, and, whilst establishing the correctness of the formula HF, demonstrated that it exhibits association similar to that shown by acetic acid and nitrogen peroxide. With Hambly, Thorpe also prepared gaseous phosphoryl trifluoride, which is produced by heating cryolite and phosphorus pentoxide, and showed it to have the molecular formula  $\text{POF}_3$ . With J. W. Rodger, the corresponding sulphur compound,  $\text{PSF}_3$ , was prepared by the action of phosphorus pentasulphide on lead fluoride. The investigation, made with A. E. H. Tutton, of the changes involved in the burning of phosphorus in a limited supply of air led to the recognition of phosphorus tetroxide, and the isolation of phosphorous oxide, the

true nature of which, as an easily fusible (melting at  $22.5^{\circ}$ ) and readily volatile compound, was established. The authors succeeded in obtaining this substance in crystalline form and showed from the vapour density the molecular weight corresponded to the formula  $P_4O_6$ . A thorough and complete examination of the physical and chemical properties of phosphorous oxide was made, and with the aid of Sir Lauder Brunton its physiological properties were studied, from which it would appear that this compound is the responsible agent in the production of match-makers' disease.

Amongst other publications of this period to be mentioned are : "The Decomposition of Carbon Disulphide by Shock" (a lecture experiment); a lecture experiment to illustrate the phenomena of coal-dust explosions; diethylphosphorous acid (with North Barker); fluosulphonic acid (with W. Kirman); and with L. M. Jones the thermal expansion of specific volumes of certain paraffins and paraffin derivatives. In 1893, the determination of the thermal expansion of liquids formed the subject of a paper read before the Chemical Society. In 1894, with J. W. Rodger, he published a paper on "The Supposed Relation between the Solubility of a Gas and the Viscosity of its Solvent," followed some years later by an account of a research on the viscosity of miscible liquids.

In March, 1894, Thorpe forsook the academic sphere to take up the post of Government Chemist, returning fifteen years later when for three years he took over the duties of Professor of General Chemistry in the Imperial College of Science and Technology. It was after his return to South Kensington that he, with A. T. Francis, made a determination of the atomic weight of strontium.

The writer is indebted to Mr. E. Grant Hooper for the following account of the Government laboratories and of Thorpe's administration and other activities whilst Director.

"This post, to which Thorpe was appointed in 1894, was instituted with the stated object of combining the chemical departments of the Inland Revenue and the Customs, then two separate Services. Both laboratories were originally founded for purely Revenue purposes, but whilst the Customs Laboratory staff continued to be occupied solely with such work, the Inland Revenue Laboratory had been invested with special functions such as Referees under the Adulteration of Food and Drugs Acts and, in addition to Revenue work, had for many years acted as the chemists and chemical advisers of nearly all the other Government Departments. Very large numbers of samples of the widest diversity had been annually examined for the Post Office, the India Office, the Admiralty, the Office of Works, and other civil establishments, and the 'Somerset House Laboratory,' as well as advising in other

capacities, had settled the specifications and examined the stores purchased for official use with the exception of explosives, which were dealt with at Woolwich. The 'Inland Revenue Laboratory,' as its official title was, had thus a very wide experience and its staff in 1894 consisted of a chief and deputy, two superintending analysts, five analysts (1st class), seven analysts (2nd class), and forty-five assistants.

"The Treasury decided that the Inland Revenue and Customs Laboratories should be united under the headship of the 'Government Chemist,' who should be paid from the Treasury Vote, although the staff in each case remained members of their original Departments. This continued for several years, but in 1911 a separate establishment, known as the Government Chemists' Department, was created, to which the staff was transferred except for a certain number of young men belonging to the now united Departments of 'Customs and Excise' and who were and are constantly employed on the more simple revenue determinations. The chemical staff at Somerset House had long outgrown its accommodation, and the development of fiscal business, demanding increased room for clerical work, necessitated the removal of the laboratory. The Treasury therefore determined to provide space elsewhere, and almost immediately after his appointment Thorpe and his staff were called upon to design a new laboratory which it was ultimately decided to build just outside Clement's Inn and closely adjacent to the Law Courts and the newer Bankruptcy Buildings. The new Laboratory, a commodious building admirably adapted for the very extensive chemical work, was brought into use in October, 1897. To this building the Inland Revenue staff was transferred, whilst the laboratory at the Custom House was continued for the examination of the more simple and routine Customs or import samples. It is probably little realised how large a proportion of the huge revenue derived from alcohol (now approximately £153,000,000) and from tobacco (now, say, £53,000,000) is really controlled by scientific work. The charging is, of course, done locally by Customs and Excise officers, but the maintenance of the regulations against the use of forbidden materials and adulteration and the checking of exact strengths or proportions wholly depend upon laboratory examination, whilst the assessment of 'drawback,' i.e., the duty returned on exportation or the allowances for waste material destroyed or denatured, is similarly a matter of purely chemical and microscopical determination. Fresh developments occur from time to time and a new method of determining the amount of dutiable ethyl alcohol in fusel oil led to Thorpe's first communication to the Chemical Society on official subjects, a

paper entitled 'The So-called Hydrates of *iso*Propyl Alcohol' (J., 1897, 71, 920), whilst reference may be made to the following papers connected with the everyday work of the laboratory, *viz.*, 'Occurrence of Paraffin in the Leaf of Tobacco' (J., 1901, 79, 982); 'Carbon Monoxide as a Product of Combustion by the Bunsen Burner' (J., 1903, 83, 874); 'Estimation of Ethyl Alcohol in Essences and Medicinal Preparations' (J., 1903, 83, 314); and 'Estimation of Methyl Alcohol in the Presence of Ethyl Alcohol' (J., 1904, 85, 1).

"Much other work either affecting the public or yielding results capable of other than merely official use was accomplished. For many years there had been a demand for duty-free alcohol which should be less objectionable and if possible cheaper than the duty-free alcohol known as methylated spirit. A committee was appointed, of which Thorpe was a member, which brought into existence what was known as 'industrial duty-free alcohol' and further provided for the special denaturing of spirit in cases where the presence of methyl alcohol or of the impurities in the crude wood spirit used for methylation was objectionable. Industrial alcohol had only half the quantity of crude wood spirit used in ordinary methylated spirit and was free from petroleum spirit, and thus was both cheaper and purer, whilst the wider use of specially denatured alcohol afforded substantial relief to many industries and to the fine chemical trade. Improved alcohol tables were also produced. The official strength of alcohols was 'that indicated by Sikes' hydrometer,' and there was no legal authority to ascertain strength in any other manner. By 7 Edward VII, c. 13, s. 4, authority was given to the Commissioners of Customs and Excise to issue regulations for ascertaining the strength of spirits in terms of the 'proof spirit' defined by 56 George III, c. 140. Tables were prepared showing the specific gravity in air at 60°/60° F. of all strengths of alcohol and the equivalent percentage of absolute alcohol by weight and by volume at 60° F. These tables, printed by the Stationery Office and available to the public, were only published after Thorpe's retirement from the Government Laboratory. Other work of a similar character was connected with sugar. Tables of the specific gravity of solutions of cane-sugar had been published by Bell, Thorpe's predecessor as chief of the Inland Revenue Laboratory, in Part I of his book 'Analysis and Adulteration of Foods,' but on the imposition of the sugar duty tables of the specific gravity of solutions of glucose were necessary to permit of the ready charging of the duty on commercial glucose—such were therefore prepared and brought into use.

"The statutory position of the Inland Revenue chemists as referees

in the case of disputed cases under the Food and Drugs Adulteration Acts has been mentioned. For many years difficulties and disputes had arisen in connexion with milk consequent upon the variation in total solids and proportion of butter fat natural to the commodity as drawn from different breeds of cow and under diverse conditions. It had always been evident that to fix a standard, although it might avoid disputes, was not all gain. On the one hand, a workable standard must be lower than the best quality milk, and it was likely that good milk would be systematically reduced to the level of a standard which might be fixed, whilst, further, the existence of a standard was all in favour of the larger organisations and against the smaller men engaged in the trade, who would probably be without chemists or other skilled assistance. In August, 1901, the Board of Agriculture laid down standards for milk solids below which milk was to be deemed adulterated unless the contrary were proved. As Chief Agriculture Analyst under the Board of Agriculture, Thorpe as chief of the Government Laboratory occupied a similar position as referee in disputed cases arising under the Fertilisers and Feeding Stuffs Acts. Just as in the case of milk under the Adulteration of Food and Drugs Acts, standards were laid down for various products and methods of analysis prescribed as the result of collaboration with a committee of representative official analysts.

"Other work connected with the Board of Agriculture may be indicated by the following Government Laboratory publications: 'Effect of feeding Cotton and Sesame Cake on Butter' (A., 1900, i, 237); 'The Fat of the Egg of the Common Fowl' (A., 1902, i, 295); 'Taxine,' the Poisonous Matter of Yew; 'Interdependence of the Physical and Chemical Criteria in the Analysis of Butter Fat' (J., 1904, 85, 248); 'A Simple Thermostat for Use in Connexion with the Refractometric Examination of Oils and Fats' (J., 1904, 85, 257); 'Analyses of Samples of Milk referred to the Government Laboratory in Connexion with the Sale of Food and Drugs Acts' (J., 1905, 87, 206).

"Two subjects of general interest to the public and on which much work was done in the Government Laboratory were connected with lead in pottery glazes and arsenic in food substances and drugs. The Factory Department of the Home Office were, of course, concerned with cases of lead poisoning in industry and especially in connexion with the pottery trade. Regulations as to employment, medical examination of workers, etc., had long been in existence, but a systematic examination of pottery glazes showed considerable variation in the proportions of lead used and in the degree of solubility of the lead, the latter largely depending upon whether

the lead was used as a readily soluble compound such as white lead or whether a fritt was first prepared and the glaze was compounded with the use of such a ground lead silicate. At first the trade as a whole considered the use of lead imperative, and even when it was shown that it was possible to use a lead silicate of a comparatively insoluble character difficulties were alleged, notwithstanding the fact that it was shown that, in addition to endangering the health of the pottery workers, there was pottery on the market which was a danger to the public users because acid fruits, mint-sauce, etc., extracted quite notable proportions of lead from the glaze. Ultimately the use of leadless glazes was proved to be quite practicable, and where lead was still employed the use of comparatively insoluble lead compounds was stimulated by the Home Office granting a relaxation of the conditions of employment in the pottery industry where glazes with a minimum lead-solubility were exclusively employed. Papers on this subject are as follows: 'Lead Silicates in Relation to Pottery Manufacture' (J., 1901, 79, 791; 1910, 97, 2282), and a lecture at the Royal Institution.

"In 1901, the world was startled by several cases of arsenical poisoning in Manchester and its neighbourhood which were proved to be due to the consumption of contaminated beer. It was ultimately proved that these cases were caused by the use of an impure, i.e., an arsenical, sulphuric acid for the conversion of starchy material into glucose, which in turn had been employed as an adjunct to malt in the brewing of beer. Extensive investigation showed that arsenic in small but appreciable proportions was widely present in beer; malt itself was found to be contaminated in many instances, such contamination arising from the presence of small quantities of arsenic in the coal and coke used for drying the malt on the malt-kilns. The Commissioners of Customs and Excise, having control over the materials used for brewing, were naturally involved and at once issued orders against the use of any material containing arsenic and against the dispatch of beer into consumption if it contained that substance. The Government Laboratory became flooded with samples from all over the United Kingdom, and a Royal Commission was appointed to investigate the subject. Lord Kelvin was Chairman and Thorpe was a member of the Commission. For the rapid determination of the presence of poisonous proportions of arsenic in beer the Reinsch test had been first used. Thorpe demanded of his staff a gravimetric method, although it was pointed out that the Marsh test afforded a ready means of determination and that the quantities of arsenic so far reported were so small that their separation by a gravimetric method from a liquid like beer, containing relatively large pro-

portions of organic matter, was likely to be difficult. Such a process was, however, worked out and evidence was given before the Royal Commission showing the actual separation of fractions of a milligram of arsenic from quantities such as a pint of beer, and the results of the examination of samples from various parts of the country were furnished. Meantime Local Government Chemists had been mainly using the Marsh test, although not without some trouble consequent on the difficulty at that time of obtaining for the hydrogen-production zinc which was itself sufficiently free both from arsenic, on the one hand, and, on the other, from impurities interfering with the regular evolution of the arseniuretted hydrogen where arsenic was present in the substance under examination. In view of these difficulties and largely under the influence of Lord Kelvin, an electrolytic Marsh test apparatus was devised at the Government Laboratory and put into use. The discovery of arsenic in beer led to an investigation of other materials, not merely brewing substances, malt and sugars, coal and coke used for drying malt, but other substances employed for various purposes, and especially drugs. The result was the revelation of the widespread distribution of arsenic in small proportion and the general recognition of the necessity of laying down standards of purity so that, if absolute freedom from arsenic were not attainable at a non-prohibitive cost, yet both the public and the manufacturers and vendors could be protected by stated maxima. In addition to the evidence published by the Royal Commission, reference may be made to the following papers on this subject: 'Estimation of Arsenic in Fuel' and 'Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials' (J., 1903, 83, 969, 974); 'Note on the Application of the Electrical Method to the Estimation of Arsenic in Wall-papers, Fabrics, etc.' (J., 1906, 89, 408).

"Another subject affecting public health and especially the health of workpeople employed in the lucifer match industry was that concerned with the presence of white phosphorus in matches. When the use of this substance was forbidden, the detection of small quantities of white phosphorus in the presence of red phosphorus or of other phosphorus compounds became a matter of importance. Hence the paper, 'Note on the Detection of White Phosphorus in the Igniting Composition of Lucifer Matches' (J., 1909, 95, 440).

"In 1907, the Austrian Government having lent to the British Royal Society certain pitchblende residues, Thorpe undertook the purification of the radium chloride and the re-determination of the atomic weight of radium. A very large number of fractional

recrystallisations of radium chloride were made in the Government Laboratory and the atomic weight 226.7 was deduced in close agreement with Madame Curie's number, 226.2 (*Proc. Roy. Soc.*, 1908, 80, A, 298)."

Thorpe took part in four eclipse expeditions, viz., that of December 22nd, 1870, in Sicily; of July, 1878, at La Junta, Colorado; of August, 28—29th, 1886, at Hog Island, Grenada, West Indies, and of August 16th, 1893, at Fundium, French Senegal. On the last two occasions observations were made on the photometric intensity of light, which formed the subject-matter of two papers published in conjunction with Capt. Abney (*Phil. Trans.*, 1889, 180, A, 368; 1896, 187, A, 423). After the eclipse expedition in 1878 he and Sir Arthur Schuster made a series of magnetic observations in America along the Fortieth Parallel, which were communicated to the Royal Society in a paper entitled, "A Magnetic Survey of the Fortieth Parallel in North America between the Atlantic Ocean and the Great Salt Lake, Utah" (*Proc. Roy. Soc.*, 1879, 29, 1; 1880, 30, 132). This was followed in 1880 by a "Note on the Determination of the Magnetic Inclination in the Azores" (*ibid.*, 1881, 31, 237).

The results of an extensive magnetic survey of the British Isles made in collaboration with his colleague, Sir Arthur Rücker, during the years 1884—1888 formed the subject of the Bakerian Lecture delivered by Thorpe in 1889 (*Phil. Trans.*, 1890, 181, A, 55); and an extension of this work, containing the records of observations at 205 stations throughout the British Isles, constitutes the volume 1896, 188, A of the *Philosophical Transactions*.

Thorpe was elected to the Royal Society in 1876, served on the Council during the years 1890—1891, 1893—1895, and 1899—1903, acted as Foreign Secretary during 1899—1903, and represented the Society on the occasion of the 200th celebration of the foundation of the Royal Academy of Sciences of Berlin. He delivered the Bakerian Lecture on two occasions, in 1889 and 1904, the results of his determination of the atomic weight of radium being the subject of the second lecture. In 1889 he was awarded a Royal Medal. The President of the Royal Society (Sir Gabriel Stokes), in making this award, spoke as follows: "Professor Thomas Edward Thorpe's experimental work has secured for him a place in the first rank of living experimentalists. His researches, which are not confined to one department of chemical science, are all distinguished both by accuracy and originality of treatment. As examples of the high character of his investigations, those of the determinations of the atomic weights of titanium and gold may be specially cited as permanently setting the value of two most important chemical



constants; whilst his researches on fluorine compounds, including the discovery of thiophosphorylfluoride, a body capable of existing undecomposed in the state of gas, and his latest work on the vapour density of hydrofluoric acid, do not fall short of the highest examples of classical chemical investigation."

It was at the Edinburgh Meeting of the British Association in 1871 that Thorpe acted as Secretary of Section B (Chemistry) and fifty years later he was President of the Association at its meeting in the same city. At the Leeds Meeting in 1890, he presided over the Chemistry Section. The Presidential Address at the Edinburgh Meeting which, owing to illness, he was unable to deliver in person, was devoted to a plea for an international ban on chemical warfare. He served on several Royal Commissions and numerous Departmental Committees, was an active member of the International Committee of Atomic Weights, contributing experimental data for the determination of the atomic weights of no fewer than six elements. In 1895 he was elected President of the Society of Chemical Industry.

The record of Thorpe's scientific investigations and achievements shows how abundantly he gave of himself without stint or reserve to the advancement of knowledge, and this with a success indicated in the many recognitions and honours received by him from universities and learned societies both at home and abroad. In 1900 he was made a C.B., and on retiring from the Directorship of the Government Laboratory was knighted. In 1912 he resigned the Chair of General Chemistry at the Imperial College of Science and Technology and went to reside at Salcombe in South Devon, where he had built a house, and there devoted himself to literary work, yachting, and gardening. Sailing remained a lasting source of pleasure to him, and it is characteristic of the man that he should use his pleasure cruises as opportunities for research, as in the case of the magnetic surveys, already mentioned. Further, his yachting experiences were made to provide the material for those literary excursions: "A Yachtsman's Guide to the Dutch Waterways" (Standford, 1905), and "The Seine from Havre to Paris" (Macmillan, 1913). The revision and enlargement of the "Dictionary of Applied Chemistry" occupied him to within a few days of the illness which, as already stated, terminated fatally on February 23rd, 1925.

As to Thorpe's influence and personality, no better testimony is needed than that expressed by Dr. Tutton in the obituary notice published in the *Proceedings of the Royal Society* in December, 1925: "An able and incisive speaker, compelling attention (in spite of his stature) both by his resonant voice and his always interesting matter, a brilliant lecturer and experimenter, a faithful teacher

who never failed to make himself clearly understood, and an original investigator of keen penetration, infinite reserve, consummate manipulative skill, scrupulous accuracy and its ever accompanying quality of neatness, Sir Edward Thorpe not only inspired those who had the good fortune to study under him, but impressed the honourable mark of thoroughness and trustworthiness on the department of British Science which he so well represented. The spirit of research ever emanated from him and vivified all his teaching, and it may be hoped, and indeed believed, that its leaven has quickened the spirit of a band of devoted students, striving to emulate his fine example and to work for the honour of British Science and the acquirement of true knowledge for its own sake, throughout the whole Empire."

In conclusion the writer wishes gratefully to acknowledge the kindness of Lady Thorpe and her niece (Miss Watts) in placing at his disposal documents relating to the life and work of Sir Edward Thorpe.

P. P. B.

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CXXXIV.—*Germanium. Part II. Germanium Tetrachloride and its Ammonia Compounds.*

By WILLIAM PUGH and JOHN SMEATH THOMAS.

GERMANIUM tetrachloride was first described by Winkler (*J. pr. Chem.*, 1886, **142**, 177), who obtained it by the action of chlorine on heated germanium. Recently, Dennis and Hance (*J. Amer. Chem. Soc.*, 1922, **44**, 304) have prepared the compound in much larger quantities by a modification of Winkler's method. The disadvantage of this mode of preparation is that it involves the prior preparation of metallic germanium, and although this can be accomplished fairly readily by the reduction of the dioxide with potassium cyanide, as described by the present authors (*J.*, 1924, **125**, 816), it seemed desirable to investigate the possibility of preparing the substance from the dioxide by a simpler and more direct process.

An attempt to prepare germanium tetrachloride by the well-known method of passing chlorine over a strongly heated mixture of the dioxide and carbon did not yield very satisfactory results. However, by the action of a mixture of carbon monoxide and chlorine, or, better still, of carbonyl chloride on strongly heated germanium dioxide, germanium tetrachloride is very readily obtained.

Ten grams of germanium dioxide were placed in a porcelain boat in a silica tube which was heated to dull redness. Carefully dried carbonyl chloride, or a mixture of carbon monoxide and chlorine in approximately equal proportions, was then passed through the tube and a rapid reaction immediately took place. The products of the reaction were passed to the bottom of a long tube terminating in a bulb, of about 15 c.c. capacity, which was immersed in a freezing mixture. From this tube moisture was excluded by means of a phosphoric oxide guard tube attached to the exit. The reaction was complete in 2 hours, only a very small quantity of a yellowish-brown residue remaining in the boat. About 10 c.c. of a greenish-yellow liquid had condensed in the receiver. The colour, due mainly to dissolved chlorine, was less pronounced when carbonyl chloride was used. The dissolved gases were removed from the crude liquid by passing a stream of dry air through it as described by Dennis and Hance (*loc. cit.*), the containing vessel being surrounded by a freezing mixture. Twenty grams of a clear, colourless, and very mobile liquid were obtained (Found: Ge, 33.6; Cl, 66.35. Calc. for  $\text{GeCl}_4$ : Ge, 33.7; Cl, 66.3%).

An experiment was next carried out in which germanium dioxide

was suspended in hot concentrated sulphuric acid through which a stream of hydrogen chloride was bubbled. It was hoped that the hydrogen chloride would react readily under these conditions with the dioxide and that the sulphuric acid would prevent hydrolysis of the resulting tetrachloride. The method did not give satisfactory results. No visible reaction occurred until the sulphuric acid had begun to fume ( $270^{\circ}$ ), but after the mixture had been kept at this temperature for several hours much of the germanium dioxide had disappeared and about 6 c.c. of distillate had collected in the well-cooled receiver. This distillate consisted of two layers, each of about equal volume. On re-distillation, the lower layer came over completely below  $75^{\circ}$ , whilst the upper layer boiled at  $107\text{--}108^{\circ}$ . The first fraction was germanium tetrachloride contaminated with hydrogen chloride. The exact nature of the heavier layer has not been determined, but the point is being investigated. It appears to be sulphuryl chloride.

In a subsequent experiment, 10 g. of pure germanium dioxide were placed in a small distilling flask with 100 c.c. of concentrated hydrochloric acid. The flask was connected with a small double-surface condenser, the delivery tube of which was drawn out to a long capillary tube which dipped to the bottom of a receiver similar to that described previously. This receiver was immersed in a freezing mixture. About 5 c.c. of concentrated sulphuric acid were placed in the receiver, and the flask was heated in a bath at  $90^{\circ}$ . During the distillation a tendency was observed for hydrolysis of the product to take place as the hydrochloric acid became less concentrated. To obviate this, a slow stream of hydrogen chloride was bubbled through the liquid while the distillation was in progress. The dioxide dissolved fairly rapidly. As soon as solution was complete, the process was stopped; a stream of dry air was passed through the well-cooled distillate for several hours in order to remove dissolved hydrogen chloride. The product was then distilled from the sulphuric acid and was collected with the usual precautions in a small distilling flask. After a further distillation, without the addition of sulphuric acid, 20.2 g. of very pure germanium tetrachloride were obtained, b. p.  $85.5^{\circ}$  (Found: Ge, 33.7; Cl, 66.3%). This proved to be the most convenient method of preparing germanium tetrachloride.\* Equally good results were obtained with germanium dioxide which had been ignited at a bright red heat as with the freshly precipitated substance.

During the distillation of germanium tetrachloride from sulphuric

\* Since this was written Tabern, Orndorff, and Dennis have described a somewhat similar method of preparing germanium tetrachloride (*J. Amer. Chem. Soc.*, 1925, 47, 2032).

acid, an interesting phenomenon was observed. The two liquids do not mix and at the ordinary temperature the tetrachloride forms the lower layer. At  $0^{\circ}$ , the interface between the two liquids is perfectly flat. As the temperature rises, this interface becomes more and more convex until at  $50^{\circ}$  the lower layer resembles an egg with the pointed end upwards. Then, quite suddenly, the position of the two layers becomes reversed, the sulphuric acid being the denser, and the liquid interface is now concave. As the temperature is raised still higher, the curvature of this interface becomes less and less until, just below the boiling point of the tetrachloride, it again becomes quite flat and exhibits a very fine play of iridescent colour. On cooling, the liquids undergo the same changes in the reverse order.

*The Action of Dry Gaseous Ammonia on Germanium Tetrachloride.  
Hexamminogermanic Chloride.*

It is well known that ammonia reacts readily with stannic chloride (Rose, *Pogg. Ann.*, 1832, 24, 109), with lead tetrachloride and with zirconium tetrachloride (Matthews, *J. Amer. Chem. Soc.*, 1899, 20, 815, 839, 843). In each case solid compounds are produced which, however, do not appear to have been fully investigated. Further work in this direction is now being carried out in these laboratories.

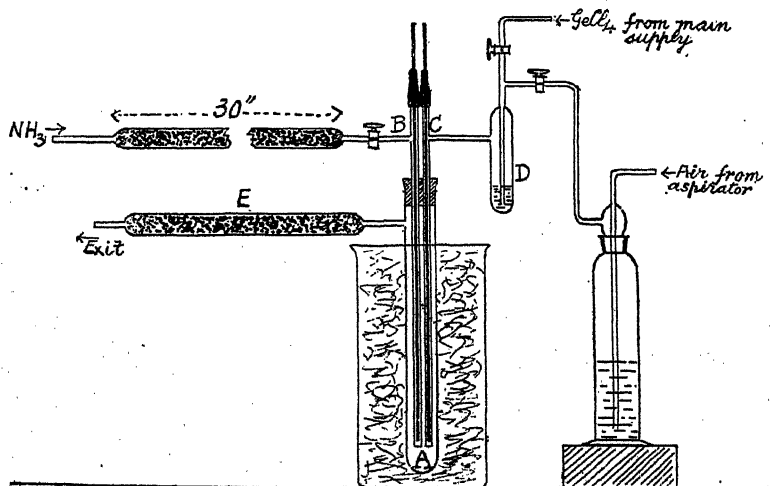
Germanium tetrachloride also combines readily with ammonia. In a preliminary experiment, dry ammonia was led on to the surface of germanium tetrachloride, cooled in a freezing mixture. A vigorous reaction took place, dense white fumes were formed, and much heat was evolved. Absorption of ammonia proceeded quietly after a time, and the passage of the gas was continued for several hours. The product was a white powder having a strong smell of ammonia which, however, disappeared after the substance had been exposed to the air for several hours (Found: Ge, 20.7; Cl, 40.75;  $\text{NH}_3$ , 24.3%. Ratio Ge : Cl = 1 : 3.99; Cl :  $\text{NH}_3$  = 1 : 1.24). Analyses of other specimens prepared in the same way yielded similar results. In every case, the ratio Ge : Cl was the same within the limits of experimental error, but the ratio Cl :  $\text{NH}_3$  varied considerably; further, from 14% to 20% of the material always remained unaccounted for.

These analytical results may, of course, be attributed to replacement of ammonia in the original ammine by water molecules derived from the moisture in the air. In order to test this possibility, a further preparation was undertaken in which every precaution was taken to exclude moisture. The apparatus employed is illustrated in Fig. 1.

The reaction vessel, A, was about 9 inches long and  $1\frac{1}{4}$  inches in

diameter. It was closed by means of a tight-fitting rubber stopper, through which passed two fairly wide tubes, *B* and *C*, which served to admit ammonia and germanium tetrachloride, respectively. In order to prevent the choking of these tubes by the product of the reaction, they were provided with thin glass rods, attached by means of rubber tubing, by the movement of which they could be cleared as necessity arose. After the apparatus had been thoroughly dried, about 1 c.c. of germanium tetrachloride was distilled into *D* from the main supply and through it a slow stream of dry air was bubbled; at the same time, *D* was heated to 50° by means of a bath of warm water. In this way, a steady stream of tetrachloride

FIG. 1.



vapour was introduced into *A*, which was kept cold by means of a freezing mixture. At the same time, dry ammonia was also admitted to the reaction vessel, the rate of flow of the gases being so regulated that a slight excess of ammonia was always present. This rate had to be slow, otherwise much of the finely divided product was carried away by the stream of air and lost. The waste gases escaped by the exit tube, *E*, which was fitted with a suitable guard tube to prevent ingress of moisture.

After all the germanium tetrachloride had been driven over, the flow of ammonia was continued for an hour to ensure complete combination and any excess, together with some adsorbed ammonia, was then removed by passing dry air through the apparatus until no smell of ammonia could be detected at the exit tube. The product was then transferred to a well-stoppered bottle and kept

over quicklime in a desiccator. It was a pure white, light, and extremely soft powder which proved to be  $\text{GeCl}_4 \cdot 6\text{NH}_3$  (Found: Ge, 22.95; Cl, 44.9;  $\text{NH}_3$ , 31.9. Ratio Ge : Cl = 1 : 3.97; Cl :  $\text{NH}_3$  = 1 : 1.49.  $\text{GeCl}_4 \cdot 6\text{NH}_3$  requires Ge, 22.8; Cl, 44.9;  $\text{NH}_3$ , 32.3%).

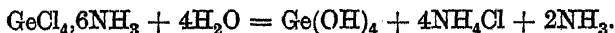
In order to obtain further information regarding the change which the hexammine undergoes when it is exposed to moist air, 2 grams of the freshly prepared substance were exposed to the action of moist carbon dioxide-free air and the change of weight was observed at frequent intervals. During the first 2 days, the weight increased rapidly; the increase then became more gradual, until after a month the weight was constant; the increase then amounted to 11.9% [Found: Ge, 20.4; Cl, 40.3;  $\text{NH}_3$ , 19.8;  $\text{H}_2\text{O}$  (diff.), 19.4%. Ratio Ge : Cl = 1 : 4.0; Cl :  $\text{NH}_3$  = 1 : 1.03]. This change in composition taken in conjunction with the observed increase of weight corresponds to the replacement of two molecules of ammonia by four molecules of water ( $\text{GeCl}_4 \cdot 4\text{NH}_3 \cdot 4\text{H}_2\text{O}$  requires Ge, 20.3; Cl, 40.1;  $\text{NH}_3$ , 19.8%, and an increase in weight of 12.03%).

According to Mendeléev (*Ber.*, 1870, 3, 422), water, in similar circumstances, replaces ammonia in pentamminocupric sulphate, molecule for molecule; from the analytical results, however, it is clear that such simple replacement does not occur in this case. Examples of the replacement of a molecule of ammonia by two molecules of water do not appear to have been observed and it may be pointed out that in this case such a replacement would involve a change in the co-ordination number of germanium, unless, indeed, double molecules of water are concerned, as Werner suggested is the case in the alums.

This replacement of ammonia by water molecules may, however, be explained in another way. Instead of replacement of ammonia according to the equation



the hexammine may undergo hydrolysis thus :



In either case, the solid product would have the same composition, and analytical methods cannot decide, therefore, which is the correct explanation. The behaviour of the substance on treatment with water points, however, to the second explanation. The hexammine itself dissolves completely in water to a clear and colourless solution which only becomes turbid after standing for several hours. A compound such as  $\text{GeCl}_4 \cdot 4\text{NH}_3 \cdot 4\text{H}_2\text{O}$  might be expected to behave in a similar way. The actual substance does

not dissolve completely in water, but leaves a residue which is readily soluble in sodium hydroxide and does not contain chlorine, a behaviour which might be expected from a mixture of ammonium chloride and hydrated germanium dioxide.

*The Action of Ammonia on Germanium Tetrachloride Dissolved in Ether.*

Germanium tetrachloride (1 c.c.) was dissolved in 100 c.c. of dry ether contained in a flask cooled in a freezing mixture, and dry ammonia was bubbled through the solution. A white precipitate at once formed and the heat of the reaction caused the ether rapidly to evaporate. The current of ammonia was continued until all the ether had thus been removed, and the white powder remaining was transferred to a bottle and stored in a desiccator over quicklime. It smelled strongly of ammonia. It was identical with the product obtained by the interaction of the gaseous substances (Found: Ge, 23.0; Cl, 44.8;  $\text{NH}_3$ , 31.85%). All the values are slightly low; this is probably accounted for by access of moisture during transference from one vessel to another.

The ammonia pressure of the hexammine is very small; a specimen was kept over concentrated sulphuric acid for a week without undergoing any appreciable change in weight. The compound is readily soluble in water, but is slowly hydrolysed in solution and the liquid becomes turbid. The solution smells strongly of ammonia. The hexammine is insoluble in ether, alcohol, chloroform and all the common organic solvents. When it is heated in dry air, the substance sublimes completely but with slight loss of ammonia. An analysis was made of a specimen which had been sublimed in a current of dry air in a specially constructed apparatus from which air was carefully excluded (Found: Ge, 23.2; Cl, 46.4;  $\text{NH}_3$ , 30.5%). Possibly a lower ammonia compound is formed at very high temperatures.

*The Interaction of Germanium Tetrachloride with some Amines.*

A number of amines being available in connexion with another investigation, the interaction of these substances with germanium tetrachloride was studied. Additive compounds with mono-, di-, and tri-ethylamine, with propylamine, and with butylamine were prepared by bringing the vapours of the two substances into contact in the same way as in the preparation of the ammonia compounds. These additive compounds were also obtained by passing amine vapour into solutions of germanium tetrachloride in ether. In every case, the product was a white powder closely resembling the hexammine both in appearance and in properties.

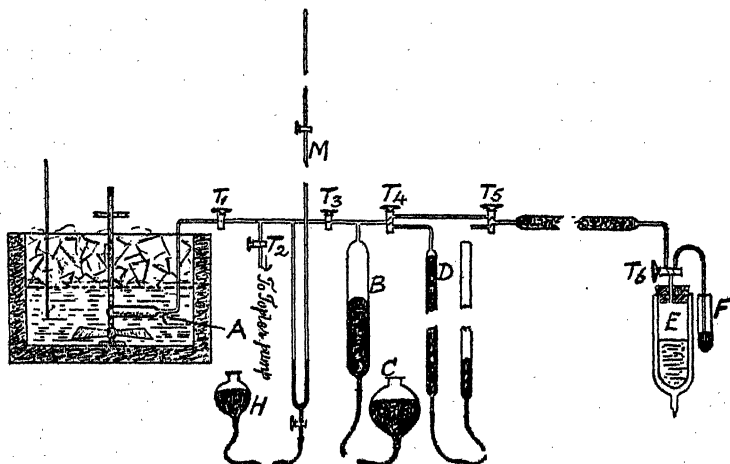


The amine derivatives are quite stable in dry air and have little or no smell. They are decomposed by moist air and under these conditions they smell strongly of the amine. They are readily soluble in water, but the solutions undergo hydrolysis and become turbid on standing. They are insoluble in the common organic solvents. They contain six molecules of amine to each molecule of the tetrachloride [Found for the diethylamine compound: Ge, 11.0; Cl, 21.7;  $(C_2H_5)_2NH$ , 67.2.  $GeCl_4 \cdot 6(C_2H_5)_2NH$  requires Ge, 11.1; Cl, 21.8;  $(C_2H_5)_2NH$ , 67.1%].

*The Existence of Higher Ammonia Derivatives of Germanium Tetrachloride.*

During the investigation of germanium tetrachloride hexamine, absorption of ammonia was observed to occur when this gas was

FIG. 2.



compressed in contact with the hexamine. In order to determine the nature of this change, a known weight of the solid was treated with ammonia under a pressure of about 3 atmospheres until no more of the gas was absorbed. Small, measured quantities of ammonia were then removed and after each such removal the equilibrium pressure was measured. Owing to the high pressures developed at higher temperatures, it was found most convenient to work at  $0^\circ$ . The apparatus employed is sketched in Fig. 2.

The hexamine (1.3756 g.), contained in a small stoppered bottle, was placed in the tube A, which was then sealed in such a way as to prevent ingress of moisture. The tap  $T_1$  being closed, the stopper of the bottle was removed by gentle shaking. After sealing A to

the remainder of the apparatus, the whole was thoroughly dried by alternately exhausting and then filling it with air which had passed over phosphoric oxide. The apparatus was then washed out several times with dry gaseous ammonia, obtained by the evaporation of liquid ammonia in the Dewar vessel, *E*, from which superfluous gas escaped by means of the mercury trap, *F*.

All the air being in this way removed, *A* was immersed in a thermostat kept at 0°, and the vessel *B*, having a capacity of 200 c.c., was filled with ammonia, which was then compressed into *A* by closing *T*<sub>2</sub> and *T*<sub>4</sub>, opening *T*<sub>1</sub> and *T*<sub>3</sub>, and raising the mercury reservoir, *C*. Under a pressure of 3 atmospheres absorption of ammonia took place very rapidly at first—600 c.c. were taken up in the first  $\frac{1}{2}$  hour. The process then became gradually slower, until eventually about 1100 c.c. of ammonia had been absorbed. By this time the substance in *A* had become liquid.

Ammonia was then removed from the reaction vessel in small quantities at a time, each amount being measured by means of the gas burette, *D*. All volumes were reduced to *N.T.P.* After each removal, the apparatus was allowed to stand until the pressure became constant. The pressure was measured by means of the manometer, *M*, which allowed of any pressure from 0 to 2400 mm. being determined. When not in use, *T*<sub>2</sub> and *T*<sub>3</sub> were sealed with mercury. All pressure measurements were made from the same point on the manometer, so that the volume of the apparatus was always the same. The amounts of ammonia and the corresponding equilibrium pressures are in Table I.

TABLE I.

Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.	Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.	Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.	Vol. of NH <sub>3</sub> removed.	<i>P</i> in mm.
0	1998	152.0	1041	553.4	1040	978.1	1040
12.9	1742	188.0	1040	586.4	1040	997.4	1040
26.3	1408	225.6	1042	634.4	1040	1018.4	814
51.0	1095	259.2	1041	682.4	1040	1026.0	720
53.6	1065	299.0	1042	716.8	1042	1040.1	522
56.0	1049	340.4	1041	767.4	1040	1049.0	425
60.3	1044	379.0	1040	812.6	1041	1063.0	295
77.1	1045	422.0	1041	854.4	1040	1087.2	95
95.3	1044	459.3	1041	896.1	1041	1105.3	0
114.8	1042	496.0	1040	936.9	1042		

From this table it is clear that only one higher ammonia compound can exist within the range of pressures examined and that the dissociation pressure of this compound at 0° is 1040 mm., that is to say, the compound cannot exist at the ordinary temperature and pressure. It is curious that this compound should be a liquid.

When all the ammonia had been removed, the volume of *A* was

determined by filling the vessel with dry air and then pumping off and measuring the volume of air used. The volume was 32 c.c. The vessel was then opened and a specimen of the solid, which had now acquired a porous structure, was analysed (Found: Ge, 22.9; Cl, 44.8;  $\text{NH}_3$ , 32.0. Calc. for  $\text{GeCl}_4 \cdot 6\text{NH}_3$ : Ge, 22.8; Cl, 44.9;  $\text{NH}_3$ , 32.3%). This proves the end-product to be the hexammine and confirms the statement made in an earlier paragraph that the ammonia pressure of this compound is extremely small.

From the quantities of ammonia removed, together with the weight of the hexammine originally taken, the formula of the higher ammine can be calculated. By a graphical method, it was estimated that the dissociation pressure of the compound was reached after the removal of 57.5 c.c. of ammonia and that the compound was completely dissociated after the removal of 1004 c.c. of the gas (both measured at *N.T.P.*). Thus, 1.3756 g. of the hexammine had combined with 946.5 c.c. of ammonia. Now the addition of each additional molecule of ammonia to the hexammine requires 96.92 c.c. of the gas, and hence, within the limits of experimental error, 10 additional molecules of ammonia have been taken up and the higher compound thus has the formula  $\text{GeCl}_4 \cdot 16\text{NH}_3$ .

The variation of the dissociation pressure of the higher compound was also investigated between the temperatures  $0^\circ$  and  $16^\circ$ . The pressures observed, which are in Table II, were found, when plotted against the temperature, to lie on a straight line. By extrapolating this curve, the dissociation pressure was found to be 760 mm. at  $-4^\circ$ .

TABLE II.

Temp. ....	$0^\circ$	$0.4^\circ$	$1.8^\circ$	$4.0^\circ$	$6.0^\circ$
Press. (mm.) ....	1040	1055	1164	1309	1462
Temp. ....	$7.9^\circ$	$9.9^\circ$	$11.9^\circ$	$13.4^\circ$	$16.1^\circ$
Press. (mm.) ....	1590	1733	1889	2001	2190

An examination of Table I shows that, in addition to the formation of the higher ammonia compound, adsorption of the gas also takes place, for neither the volume of ammonia removed in reducing the pressure from 1998 mm. to the equilibrium pressure nor the volume pumped off after the complete dissociation of the higher compound is in agreement with that calculated by means of the gas laws. The discrepancy was far greater at low pressures, for, whilst the removal of 57.5 c.c. of ammonia (measured at *N.T.P.*) reduced the pressure from 1998 mm. to 1040 mm., the ammonia remaining after the higher compound had completely dissociated occupied 101.3 c.c. under the same conditions. Thus it appears that adsorption of ammonia occurs to a greater extent at low pressures.

This abnormality is, however, easily explained by the fact that

$\text{GeCl}_4 \cdot 16\text{NH}_3$ , being liquid, exposes a comparatively small surface, whereas the hexammine produced by its dissociation is rendered extremely porous by the escape of ammonia during the process of dissociation.

The constitution of the hexammine is readily explained by means of Werner's co-ordination theory if the co-ordination number of germanium is taken to be 6 and the whole of the chlorine is ionisable. It is, however, somewhat difficult to reconcile this with the electron theory of valency. According to Langmuir's theory, the germanium atom (atomic number 32) has 2, 8, 8, 14 electrons in the various shells and requires 4 electrons to bring the number of electrons in the outer shell up to that of the inert gas immediately following. In the hexammine, the central atom  $[\text{Ge}(\text{NH}_3)_6]^{++++}$  must therefore have an outer shell of 22 electrons. But such a compound should be unstable and should readily lose ammonia, as do the solid hexammines of zinc, nickel, and copper. So far from this being the case, germanium tetrachloride hexammine is remarkably stable and shows no tendency to lose ammonia when kept free from moisture, although, on the addition of water, ammonia is immediately liberated. Possibly a tetrammine complex is formed in solution, but the rapidity with which hydrolysis takes place makes the investigation of this point difficult.

As yet no adequate explanation of the constitution of this substance, and still less of that of the higher compound, can be offered, but the nature of these compounds and also the ammonia derivatives of the tetrachlorides of tin and lead are being further investigated.

#### *Summary.*

1. Various methods for the preparation of germanium tetrachloride have been investigated. By the action of hydrogen chloride on germanium dioxide in concentrated hydrochloric acid, under suitable conditions, the compound may readily be obtained pure.

2. The action of gaseous ammonia on germanium tetrachloride vapour and also on a solution of the compound in ether has been investigated. In each case the compound  $\text{GeCl}_4 \cdot 6\text{NH}_3$  is produced. Amines react in a similar manner.

3. Hexamminogermanic chloride is a white, very light powder which is very stable in dry air but is hydrolysed by moist air, a residue of hydrated germanium dioxide and ammonium chloride remaining. The hexammine dissolves readily in water, but becomes turbid after a time owing to separation of hydrated germanium dioxide produced by hydrolysis of the compound.

4. The hexammine when treated with ammonia under pressure absorbs the gas readily at low temperatures. A higher compound,

$\text{GeCl}_4 \cdot 16\text{NH}_3$ , is produced which is a liquid at  $0^\circ$  and has a dissociation pressure of 1040 mm. at  $0^\circ$ , 2085 mm. at  $15^\circ$ , and 760 mm. at  $-4^\circ$ .

5. No evidence of any other ammonia compound was obtained.  $\text{GeCl}_4 \cdot 16\text{NH}_3$  dissociates directly to the hexammine, which is extremely stable, having no measurable ammonia pressure at  $0^\circ$ . At this temperature, it can be kept over concentrated sulphuric acid for days without losing weight.

6. The application to these compounds of the co-ordination theory and of the electron theory of valency is briefly discussed.

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### CXXXV.—The Binary System Barium Iodide-Water.

By JOHN PACKER and ALBERT CHERBURY DAVID RIVETT.

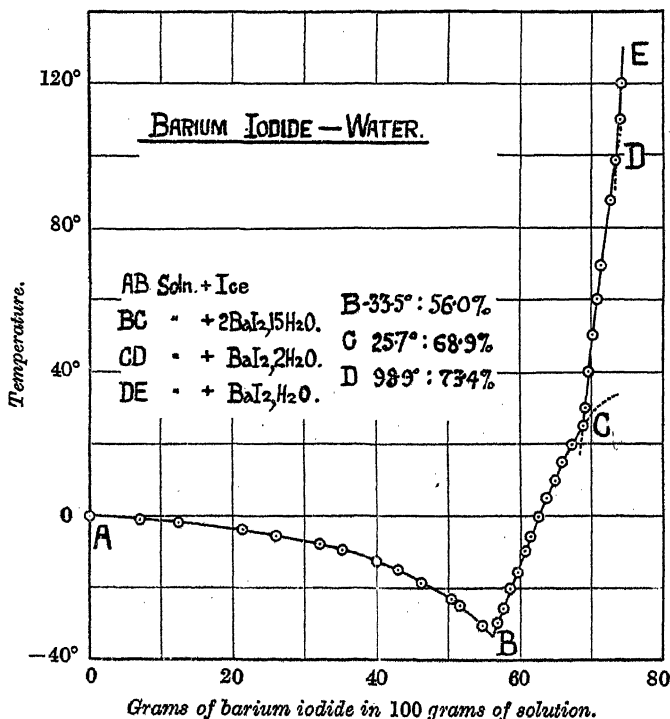
HAVING had occasion recently to seek information regarding the solubility of barium iodide in water at three or four temperatures, we found the available figures scanty and uncertain and were obliged to make new measurements. It seemed worth while to supplement these and to place on record the full binary system from the eutectic temperature ( $-33.5^\circ$ ) to  $120^\circ$ .

#### Barium Iodide-Water.

Temp.	$D_4^{20}$	% $\text{BaI}_2$ in soln.	Solid phases.	Temp.	$D_4^{20}$	% $\text{BaI}_2$ in soln.	Solid phases.
$-1.0^\circ$	1.060	7.00	Ice	$-5.8^\circ$	2.036	61.45	$2\text{BaI}_2 \cdot 15\text{H}_2\text{O}$
$-1.7^\circ$	1.117	12.4	"	$0.0^\circ$	2.071	62.5	"
$-3.7^\circ$	1.221	21.35	"	$+5.0^\circ$	2.105	63.6	"
$-5.35^\circ$	1.281	26.05	"	$10.0^\circ$	2.144	64.8	"
$-7.75^\circ$	1.371	32.05	"	$15.0^\circ$	2.176	65.75	"
$-9.35^\circ$	1.423	35.15	"	$19.9^\circ$	2.222	67.15	"
$-12.35^\circ$	1.507	39.90	"	$25.0^\circ$	2.277	68.8	"
$-14.95^\circ$	1.568	42.95	"	$25.7^\circ$	—	68.9	$2\text{BaI}_2 \cdot 15\text{H}_2\text{O}$ and $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$
$-18.15^\circ$	1.634	46.1	"				$\text{BaI}_2 \cdot 2\text{H}_2\text{O}$
$-22.9^\circ$	1.731	50.4	"	$26.0^\circ$	2.282	68.9	$\text{BaI}_2 \cdot 2\text{H}_2\text{O}$
$-24.6^\circ$	1.764	51.5	"	$30.0^\circ$	2.287	69.1	"
$-30.2^\circ$	1.842	54.6	"	$40.0^\circ$	2.304	69.6	"
$-33.5^\circ$	—	56.0	Ice and $2\text{BaI}_2 \cdot 15\text{H}_2\text{O}$ (extrapolated eutectic)	$50.0^\circ$	2.32	70.1	"
			$2\text{BaI}_2 \cdot 15\text{H}_2\text{O}$	$60.0^\circ$	2.331	70.7	"
$-29.75^\circ$	1.905	56.8	"	$69.5^\circ$	2.35	71.15	"
$-25.4^\circ$	1.927	57.5	"	$87.7^\circ$	—	72.55	"
$-20.0^\circ$	1.952	58.6	"	$98.9^\circ$	—	73.35	$\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaI}_2 \cdot \text{H}_2\text{O}$
$-15.4^\circ$	1.983	59.65	"				$\text{BaI}_2 \cdot \text{H}_2\text{O}$
$-9.7^\circ$	2.012	60.65	"	$110.0^\circ$	—	74.0	$\text{BaI}_2 \cdot \text{H}_2\text{O}$
				$120.0^\circ$	—	74.3	"

Commercial (B.D.H.) barium iodide, approximating in composition to  $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ , was purified by crystallisation, and used, as the hydrate  $2\text{BaI}_2 \cdot 15\text{H}_2\text{O}$ . The procedure adopted in examining the

system followed the usual lines. Concentrations were determined by estimating iodide volumetrically against silver nitrate, with ferric thiocyanate as indicator: they are expressed in the table as weights of anhydrous salt in 100 g. of solution. In some cases, the values were checked by estimations of barium as sulphate. Transition points were measured thermometrically and confirmed by intersections of extrapolated curves.



The mono- and di-hydrates are well known, whilst hydrates with six and seven molecules of water have been stated to exist. It is difficult to obtain a deliquescent hydrate, like the highest in this series, in a sufficiently pure state for analysis. Probably the surest procedure is to investigate it by the method depending on analysis of wet solids in a suitable ternary system, and this we have done in the system barium iodide-iodine-water, which we hope shortly to describe. The highest hydrate appears to be  $2\text{BaI}_2 \cdot 15\text{H}_2\text{O}$ , and we have not found either hexa- or hepta-hydrate.

The table and figure indicate all details of the system.

CXXXVI.—*The Constitution of Magnesium Acetate Solutions.*

By ALBERT CHERBURY DAVID RIVETT.

THE constitution of basic beryllium acetate (Urbain and Lacombe, *Compt. rend.*, 1901, **133**, 874; Bragg, *Nature*, 1923, **111**, 532; Sidgwick, *ibid.*, 808; Bragg and Morgan, *Proc. Roy. Soc.*, 1923, *A*, **104**, 437) is explicable in terms of a marked tendency on the part of the beryllium atom to exercise a co-ordination number of 4 in its linkings with oxygen. The readiness with which this occurs may be connected with the fact that the outer electrons in the atoms of beryllium and oxygen are at similar energy levels: there may thus be a decreasing tendency towards such linkings with oxygen as one passes down Group II of the Periodic Classification through magnesium, calcium, strontium, and barium. In magnesium acetate one might expect to find, at any rate, an appreciable tendency for the formation of a compound analogous to the basic beryllium salt.

In preparing hydrated magnesium acetate from magnesium oxide, acetic acid, and water, with a view to seek such a basic acetate in the ternary system oxide-acetate-water, one was struck by the ease with which supersaturated solutions could be formed, by the slow rate of their crystallisation after seeding, and by the very high viscosity possessed by solutions above a certain range of concentration. Measurements of some of the properties of these solutions have therefore been made, and from them it seems that some guidance may be obtained as to the probable condition of magnesium acetate in solutions of varying concentrations.

## EXPERIMENTAL.

The solid salt used was prepared from magnesium oxide (B. D. H.), free from sulphur, and excess of acetic acid (A. R.) diluted about fourfold with water. The crystals formed were separated on a silver gauze basket in a centrifuge of 6-inch radius at 1800 r.p.m., and kept for some weeks in a vacuum desiccator over concentrated caustic soda to remove excess acetic acid. Analysis showed them to be  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ .

All solutions were analysed by conversion of dissolved salt into anhydrous magnesium sulphate and weighing as such. Compositions of solutions are given throughout the sequel in percentages of anhydrous salt by weight; but, in the discussion, concentrations are usually quoted in g.-mols. per 1000 g. of water ( $M_w$ ) or g.-mols. per litre at 25° ( $M_v$ ).

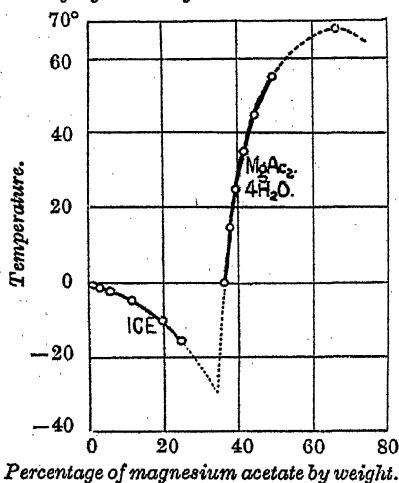
TABLE I.

## Binary System Magnesium Acetate-Water.

<i>t.</i>	% anhyd. salt.	$M_w$ .	$\Delta/M_w$ .	Solid phase.
-0.364°	1.068	0.0758	4.80	Ice.
-0.531	1.804	0.1290	(4.12)	"
-1.083	3.08	0.2232	4.85	"
-2.179	5.92	0.442	4.93	"
-4.687	11.45	0.908	5.16	"
-9.99	19.81	1.735	5.76	"
-15.23	25.0	2.345	6.52	"
-29 (extrap.)	34.5	3.70	7.8	Ice and $MgAc_2 \cdot 4H_2O$ .
+ 0.1°	36.2	3.986		$MgAc_2 \cdot 4H_2O$ .
+ 14.9	37.97	4.300		"
24.9	39.61	4.607		"
35.0	41.78	5.041		"
45.0	44.76	5.691		"
55.0	49.46	6.874		"
68±	66.4	—		(Approx. m. p. of hydrate.)

Table I gives the binary system acetate-water (plotted in Fig. 1) so far as it has been possible to determine it. On the ice curve,

FIG. 1.  
Binary system magnesium acetate-water.



solutions in the region of 30% by weight are so viscous that the phase-reaction between ice and solution proceeds too slowly for accurate measurements. On the salt-solution curve, hydrolysis sets an upper limit. The solid hydrate begins to melt at about 68°, so that this curve reaches a maximum somewhere near that temperature, as indicated by the dotted extension in Fig. 1. An extrapolation of ice and salt curves downwards points to a eutectic temperature (hydrate-ice-solution) of about -29°: but a figure so obtained is very uncertain.

Table II gives the viscosities of solutions of magnesium acetate (and a few, for comparison, at high concentrations of magnesium chloride and sodium acetate) at 25° relatively to water taken as unity. They have been measured in viscosimeters of the Ostwald pattern with time of water-flow of about 3 minutes. Pyknometers of 5 c.c. were used for determinations of density.



TABLE II.

Relative Viscosities at 25° (water = unity).

% Anhyd. salt.	$M_w$ .	$M_v$ .	$D$ .	Relative viscosity.
$Mg(C_2H_3O_2)_2$				
6.19	0.463	0.450	1.0345	1.466
13.27	1.075	1.002	1.0754	2.421
20.14	1.772	1.579	1.1160	4.325
24.51	2.280	1.966	1.1422	6.593
28.80	2.841	2.365	1.1692	10.83
32.65	3.405	2.742	1.1954	18.69
36.01	3.953	3.075	1.216	31.78
36.58	4.051	3.137	1.221	35.02
38.72	4.438	3.355	1.234	53.83
40.20	4.721	3.514	1.245	72.7
41.14	4.909	3.609	1.249	84.2
41.91	5.067	3.694	1.255	104.35
42.67	5.228	3.777	1.261	125.3
43.63	5.436	3.877	1.265	155.2
$MgCl_2$				
17.90	2.289	2.172	1.1553	2.379
25.02	3.503	3.217	1.2247	3.952
31.79	4.893	4.322	1.2952	7.737
$[Na(C_2H_3O_2)]_2$				
21.05	1.625	1.427	1.1119	2.628
31.71	2.831	2.264	1.1716	5.195

Table III includes measurements for certain solutions at temperatures from 25° to 55°, to give indications of the temperature coefficients of viscosity.

TABLE III.

Relative Viscosities at Different Temperatures.

Solution A 18.44%,  $M_w$  1.588; B 41.38%,  $M_w$  4.958; C 45.95%,  $M_w$  5.970.

Temperature.	$D$ .			Relative viscosity.		
	A.	B.	C.	A.	B.	C.
25.0°	1.1057	1.2515	—	3.73	92.9	Soln. crysd.
35.1	1.1050	1.249	1.2780	3.395	62.3	187.6
45.0	1.1048	1.247	1.2757	3.15	45.0	115.6
55.0	1.105	1.246	1.2744	2.93	34.1	78.05

In Table IV are the specific conductivities ( $\text{ohm}^{-1} \text{ cm}^{-1}$ ) at 18° and 25° measured in a cell of the form shown in Fig. 4. The total volume of the cell is 400 c.c., that of the lower tube,  $a$ , being 15 c.c. This is a useful shape when a series of dilutions is to be examined, since, provided that the lower tube be filled, the resistance of a solution is independent of the volume taken. Successive dilutions were effected by additions of water from a weight burette.

Table V shows the way in which the conductivity of a highly concentrated solution ( $M_w = 5.5$ ) varies with temperature.

TABLE IV.

Specific Conductivities ( $\text{ohm}^{-1} \text{ cm}^{-1}$ ) of Magnesium Acetate Solutions at  $25^\circ$  and  $18^\circ$ .

% Anhyd. salt.	$M_w$ .	$M_v$ .	$\kappa \times 10^3$ .		$\frac{100(\kappa_{25} - \kappa_{18})}{7 \times \kappa_{18}}$
			$25^\circ$ .	$18^\circ$ .	
3.55	0.259	0.255	19.97	17.06	2.44
5.64	0.420	0.409	26.28	22.38	2.49
7.45	0.565	0.546	30.10	25.55	2.54
9.31	0.721	0.688	32.67	27.67	2.58
11.63	0.924	0.871	34.36	28.94	2.67
14.04	1.147	1.065	34.67	29.02	2.78
18.70	1.616	1.389	32.12	26.44	3.07
23.41	2.147	1.868	26.69	21.53	3.42
28.21	2.760	2.309	19.84	15.50	4.00
33.08	3.472	2.782	12.89	9.68	4.74
37.95	4.295	3.276	7.11	5.05	5.83
43.93	5.503	3.872	2.58	1.69	7.53

TABLE V.

Specific Conductivity of a 43.9% ( $M_w = 5.50$ )-Solution of Magnesium Acetate at Various Temperatures.

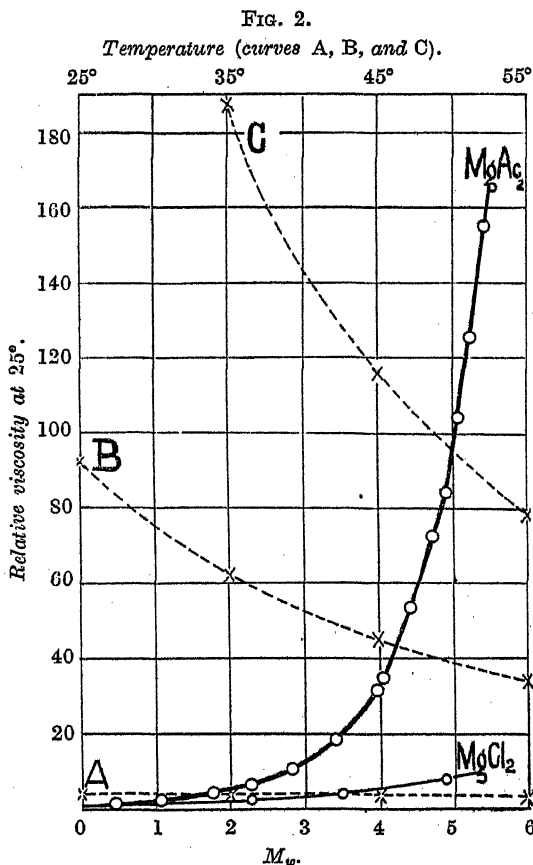
$t^\circ (\pm 0.05^\circ)$ ....	55.1	49.7	44.95	40.0	35.8	29.8	25.0	18.0	12.7
$\kappa \times 10^3$ .....	10.02	8.26	6.28	5.58	4.60	3.38	2.58	1.69	1.16

### Discussion.

Fig. 2 shows the remarkable rapidity with which viscosity at  $25^\circ$  increases with concentration. No simple equation has been found to cover the relation between the two. Rapid rise begins at about  $2.5M_w$ , the value relative to water as unity increasing from approximately 7 at that concentration to 155 at  $M_w = 5.4$  ( $M_v = 3.9$ ), a supersaturated solution. One might suppose this great change to be due to hydration of the salt, the amount of free solvent water becoming steadily less. The evidence is, however, rather contrary to any such supposition. Thus, ease of hydration is doubtless, to some extent, a characteristic of both radicals of the salt, yet neither magnesium chloride nor sodium acetate shows anything approaching the behaviour of magnesium acetate. At  $4.5M_w$ , the former has a relative viscosity of only about 9: the latter, at  $2.5M_w$ , (calculated on a doubled formula), the maximum concentration attainable, has the value 5.5. There is no indication in either case that a rapid rise is likely.

Further, if the production of heavily hydrated molecules were the cause of the high viscosity of magnesium acetate solutions compared with those of magnesium chloride, one would expect the curve of the molecular lowering of freezing point of the former to lie well above that of the latter. Fig. 3 shows how very far

this is from being the case. The figures for magnesium chloride at the dilute end are by the author (*Z. physikal. Chem.*, 1912, **80**, 546), while those for concentrated solutions are taken from the Landolt-Börnstein "Tabellen." In infinitely dilute solution a lowering of  $3 \times 1.85^\circ$  is to be expected for a ternary electrolyte fully dissociated. As concentration increases, the lowering diminishes with decreasing dissociation and then, as is usual, passes



through a minimum and begins to rise. This rise is commonly attributed, in part at least, to removal of solvent by hydration of solute. With magnesium chloride it becomes very great, exceeding  $12^\circ$  at  $2.7M_w$ ; with the acetate it is only  $6.5^\circ$  at  $2.35M_w$ . If the extrapolation in Fig. 1 to a eutectic at  $-29^\circ$  and 34.5% anhydrous salt ( $M_w = 3.7$ ) is correct, the molecular lowering at that temperature is only  $7.8^\circ$ ; but one cannot be sure of this figure. Thus

the relation to magnesium chloride is incompatible with an assumption that the acetate is the more highly hydrated, and it appears that the increase in viscosity in concentrated solutions of the latter is due to some other property of the magnesium and acetate radicals in conjunction.

A plausible suggestion is that as one passes from relatively dilute solutions, where ionic dissociation is considerable, there is an increasing tendency for association of molecules to occur, such association being the result of chelate ring-formation by means of the magnesium atom exercising a co-ordination number of 4 towards oxygen atoms. In a single molecule, such a structure as  $\text{H}_3\text{C}\cdot\text{C}\begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \cdots \text{Mg} \begin{smallmatrix} \diagdown \text{O} \\ \diagup \text{O} \end{smallmatrix} \cdots \text{C}\cdot\text{CH}_3$ , with four-atom rings, is not likely to

FIG. 3.

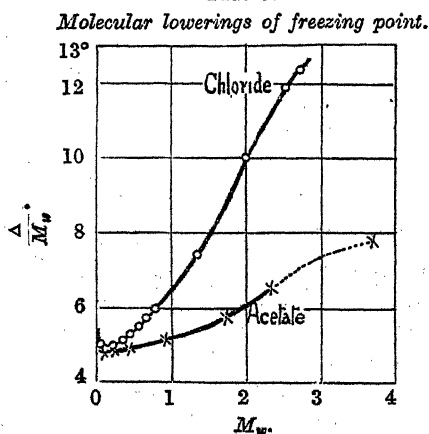
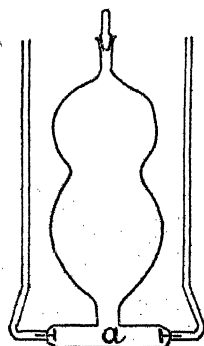


FIG. 4.



be stable, particularly in dilute solution where ionisation is considerable; but, with increase of concentration, polymerisation may occur to an indefinite extent with production of such chains as  $\text{---Mg}\begin{smallmatrix} \diagup \text{A} \\ \diagdown \text{A} \end{smallmatrix} \text{---Mg}\begin{smallmatrix} \diagup \text{A} \\ \diagdown \text{A} \end{smallmatrix} \text{---Mg}\begin{smallmatrix} \diagup \text{A} \\ \diagdown \text{A} \end{smallmatrix} \text{---Mg}\begin{smallmatrix} \diagup \text{A} \\ \diagdown \text{A} \end{smallmatrix} \text{---}$  where each unit in the chain

(straight or branched) is  $\text{---Mg}\begin{smallmatrix} \diagup \text{O}=\text{C}(\text{CH}_3)-\text{O} \\ \diagdown \text{O}-\text{C}(\text{CH}_3)=\text{O} \end{smallmatrix} \text{---}$ , a magnesium atom being linked by a co-valence to a doubly-linked oxygen atom of an acetate radical other than that originally attached to itself. It is a simple matter to draw possible spatial structures for di-, tri-, and higher molecular aggregates. Such polymerisation is of a type similar to that which apparently is shown by basic beryllium acetate.

Chains of this kind will no doubt contribute very greatly to the viscosity of a solution and might well account for the values recorded

at high concentrations. If now there is such a progressive alteration in the constitution of solute, from simple ionised salt to more or less highly polymerised molecules, there should be marked differences in the effects of temperature upon differing concentrations. At higher concentrations, increase of temperature, by promoting dissociation, should have a much greater effect upon viscosity, for instance, than it will have at lower concentrations where there is little or no polymerisation. The measurements of Table III, shown in the broken lines of Fig. 2, prove quite definitely that this is the case. Three solutions have been measured at several temperatures and each viscosity has again been expressed relatively to water at the same temperature. For an 18.4% ( $1.805M_w$ ) solution the curve (A, Fig. 2) is almost horizontal; for 46% ( $5.97M_w$ ) it (C) is very steep, and the lower the temperature the steeper is the gradient.

The measurements of specific conductivity (Table IV) show the usual maximum as concentration increases, but whereas this occurs at  $2.5M_w$  with magnesium chloride, it is at under  $1M_w$  with magnesium acetate, the conductivity being only one-fifth of the corresponding value for the former. It is idle, on the basis of conductivity work, to attempt comparisons of dissociation and ionic concentrations in cases like these, where one cannot be certain that the ions are the same in concentrated as in dilute solutions, and where any allowance for viscosity can be nothing more than conjecture. Some interest, however, attaches to the temperature coefficient of the conductivity. Values at both  $18^\circ$  and  $25^\circ$  are included in Table IV, so that for each solution one can obtain the mean percentage increase in conductivity per degree between these two temperatures. The values of  $100(\kappa_{25} - \kappa_{18})/7 \times \kappa_{18}$  are given in the sixth column of the table. Up to about  $1M_w$  the increase is close to 2.5% per degree—quite a normal figure for salts—but the coefficient continues to grow at an increasing rate as concentration rises, reaching 7%, and rising rapidly, at  $5.5M_w$ . Here again magnesium acetate furnishes an unusual case and an assumption of polymerisation leads to a qualitative explanation. Dissociation of polymerides with rising temperature will increase the number of simple molecules, which presumably are much more capable of ionisation, and so give increased conductivity: here also, however, it is unfortunate that one cannot deduct the effect, if any, due to change of viscosity between  $18^\circ$  and  $25^\circ$ .

Keeping to one and the same highly concentrated solution, containing 43.9% of anhydrous acetate ( $M_w = 5.50$ ;  $M_v = 3.87$ ) the figures of Table V show how conductivity varies over a wider range of temperature ( $12.7^\circ$  to  $55.1^\circ$ ). This solution is saturated

at 45°, but may be kept indefinitely at room temperature. Between the temperatures mentioned, the conductivity changes by more than 850% of its initial value—a very high figure for a salt. The rate of increase of conductivity with temperature is greater at higher temperatures, but the relative increase in value per degree is greater at the lower temperatures.

While this high temperature coefficient may simply reflect altered mobility consequent upon altered viscosity, it is more probable that both viscosity and conductivity changes are due to a common cause, polymerisation, which is highly sensitive to temperature change.

Some approximate measurements of surface tension have been made by the capillary tube method at 25°. There would seem to be little difference between the surface tensions of water and magnesium acetate solutions. Multiplying each rise by the density of the solution and dividing by the rise of pure water in the same tube, the following relative figures were obtained:

% anhyd. $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$	6.01	14.0	23.5	23.6	31.4	39.3
S .....	1.013	1.006	1.002	1.001	0.980	0.968

No great accuracy is claimed for the figures and the third decimal place may be incorrect by several units, but it appears fairly certain that there is an initial rise, as is usual with salts, which is followed by a decrease to less than the value for water: at none of the concentrations examined does the change in surface tension due to the presence of the salt exceed a few parts per cent.

There are other physical properties of these solutions which will be investigated later and a comparison will be made with the acetates of calcium, strontium, and barium, the higher positivity of the atoms of which will presumably involve less tendency towards formation of polymers by non-polar linkages of the type so markedly shown by beryllium, and apparently still characteristic in magnesium.

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## CXXXVII.—*The Nitration of Benzil.*

By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY  
COULSON.

ALTHOUGH benzil is scarcely attacked by ordinary strong nitric acid, it is readily nitrated by fuming nitric acid. The reaction was first carried out by Zinin (*Annalen*, 1864, Suppl. 3, 153), who recognised that a new compound distinct from benzil and *p*-nitrobenzil was formed, but did not pursue the investigation further.

It was next studied by Zagumenny (*J. Russ. Phys. Chem. Soc.*, 1872, 4, 278), who, by crystallising the crude viscid product from alcohol, obtained a moss-like mass of irregular needles melting at 107°, in which after some weeks two different kinds of crystals made their appearance and could be picked out. He thus obtained two substances crystallising respectively in yellow octahedra, m. p. 131°, and in faintly yellow, rectangular plates, m. p. 147°. Analyses showed that all these substances had the composition of dinitrobenzil, but Zagumenny expressed no opinion as to their nature. His observations were apparently overlooked, for much later Klinger and Martinoff (*Annalen*, 1912, 389, 232) claim to have obtained an almost theoretical yield of pure *mm'*-dinitrobenzil, m. p. 108·5—109°, by nitrating benzil with a large excess of cold fuming nitric acid, and more recently Barnett and Kay (*Chem. News*, 1922, 125, 57), after remarking that the preparation of dinitrobenzil is much simpler than would be gathered from the literature, state that a nearly theoretical yield of practically pure *mm'*-dinitrobenzil, m. p. 109°, can be obtained by dissolving or suspending benzil in concentrated sulphuric acid and adding slowly an equal weight of potassium nitrate.

The products described by Zagumenny (m. p. 107°), by Klinger and Martinoff (m. p. 108·5—109°), and by Barnett and Kay (m. p. 109°) appear from their melting points to have been the same, and a re-examination of the crude substances obtained by each of the three methods proves that they are substantially identical.

A closer examination of the nitration product, however, shows that it is not a single substance but a mixture of at least three isomeric dinitrobenzils. These have been separated, mainly by fractional recrystallisation, but partly by mechanical assortment of the crystals.

The crude nitration product, which melts not very sharply at about 107°, has been thus shown to consist of approximately 70% of *mm'*-dinitrobenzil, m. p. 132°, 20% of *om'*-dinitrobenzil, m. p. 149°, and about 10% of *oo'*-dinitrobenzil, m. p. 208°.

The constitutions of the first two isomerides have been established by their oxidation to the corresponding nitrobenzoic acids, whilst the third has been shown to be identical with the *oo'*-dinitrobenzil obtained by Kliegl and Haas (*Ber.*, 1911, 44, 1213) by the oxidation of *oo'*-dinitrotolane.

#### EXPERIMENTAL.

*Nitration of Benzil.*—Preliminary experiments in which benzil was heated with fuming nitric acid as described by Zagumenny showed that the product very closely resembled those obtained

when the nitration was effected by a large excess of cold fuming nitric acid as described by Klinger and Martinoff or by a mixture of cold strong sulphuric acid and potassium nitrate as described by Barnett and Kay. The crude products were identical in appearance, and the moss-like, fluffy crystals obtained by cooling saturated solutions in boiling alcohol had a similar appearance and were of approximately the same melting point, although this varied somewhat and was never sharp. All three products were similar mixtures of isomerides. The behaviours of the moss-like masses of yellow crystals, which separated when solutions of the crude products in boiling alcohol were cooled, on recrystallisation from acetone were similar, and the proportions of the various constituents of the mixture, separated as described later, were as far as could be judged about the same.

*Preparation of the Crude Mixture of Isomeric Dinitrobenzils.*—Benzil (120 g.) and 240 g. of nitric acid ( $d$  1.52) were slowly heated in a litre Jena flask with a ground-in air condenser and allowed to boil gently for about 5 hours. The mixture was then poured on to crushed ice, when a viscid, yellow mass separated. The aqueous supernatant liquid was decanted off and the yellow product, which collected together and could be easily separated, was repeatedly extracted with boiling water. In this way the nitrobenzoic acids formed as by-products were removed. The warm, yellow, plastic mass was then drained as completely as possible and allowed to cool, when it slowly solidified. The yield of crude product was about 150 g. (about 80% of the theoretical). The dry product was finely powdered and dissolved in boiling acetone. On cooling, a moss-like, crystalline mass separated in which larger, definitely-shaped crystals slowly made their appearance. On allowing the crystalline mass to remain for some days in the mother-liquor at the ordinary temperature, the quantity of compact crystals appeared to increase, and under the microscope they were seen to be of different kinds.

The whole crude product was therefore systematically fractionally crystallised from acetone and was thus separated into three fractions of very different appearance and solubility.

The three fractions were finally repeatedly crystallised until their behaviour and appearance remained unchanged after several crystallisations from different solvents. The least soluble fraction was *oo'*-dinitrobenzil, the fraction of intermediate solubility was *om'*-dinitrobenzil, whilst the most soluble constituent was *mm'*-dinitrobenzil.

*mm'*-Dinitrobenzil,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , is moderately easily soluble in boiling alcohol and very easily soluble in boiling



acetic acid, benzene, chloroform, or acetone. It separates from each of these solvents in tufts of pale yellow, irregular, slender, prismatic crystals, m. p. 132°. These crystals in the mother-liquor have a moss-like appearance (Found: C, 56.2; H, 2.8; N, 9.5. Calc. for  $C_{14}H_8O_6N_2$ , C, 56.0; H, 2.7; N, 9.3%). When dissolved in boiling acetic acid and oxidised by adding chromic acid from time to time, it is converted into *m*-nitrobenzoic acid only (yield 52–55% of the theoretical).

*om'*-Dinitrobenzil is much less soluble in all solvents than the *mm'*-isomeride, but is somewhat more soluble than the *oo'*-isomeride. It is sparingly soluble in boiling acetic acid, chloroform, benzene, or acetone, and separates from the last in pale yellow, short, compact, six-sided prisms, m. p. 149°, showing a tendency to aggregate in warty-looking crusts. The crystals are phototropic and on exposure to light assume a green colour (Found: C, 56.0; H, 2.7; N, 9.4%). On oxidation by chromic acid, a mixture of *m*- and *o*-nitrobenzoic acids was obtained.

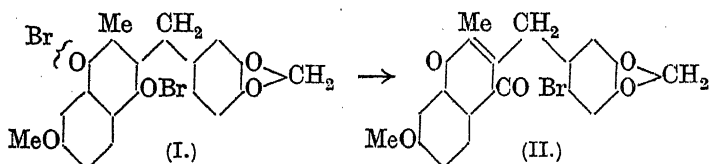
In the early stages of the fractional crystallisation of the crude product of intermediate solubility, clear, transparent crystals of a much deeper shade of yellow than the others make their appearance. These apparently are the crystals described as yellow octahedra by Zagumenny. In spite of their characteristic shape and colour, however, they prove to be, not a fourth isomeride, but mixed crystals containing the *oo'*- and the *mm'*-isomerides. On heating, they soften at about 129°, but do not melt completely till a temperature in the neighbourhood of 190° is reached, and if recrystallised from acetone can be separated into *mm'*-dinitrobenzil and *oo'*-dinitrobenzil.

*oo'*-Dinitrobenzil is very sparingly soluble in boiling alcohol and only sparingly soluble in boiling acetone, acetic acid, chloroform, or benzene. From solutions in these solvents, it separates in small, compact, pale yellow, six-sided prisms with basal ends, m. p. 208° (Found: C, 55.9; H, 2.8; N, 9.2%). It is phototropic and becomes green when exposed to light. It is scarcely attacked by chromic acid and can be recovered practically unchanged after prolonged boiling with chromic acid in acetic acid solution. Its constitution was established by comparing it with *oo'*-dinitrobenzil prepared by the oxidation of *oo'*-dinitrotolane (Kliegl and Haas, *loc. cit.*). The two specimens were identical in colour, appearance, and properties. They melted at the same temperature, 208°, alone and when mixed together, and were similarly phototropic and resistant to oxidation.

CXXXVIII.—*Synthesis of 7-Methoxy-3-(6'-bromohomopiperonyl)-2-methyl-1 : 4-benzopyrone.*

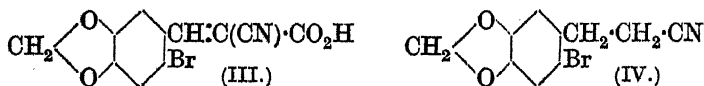
By WILSON BAKER.

BAKER and ROBINSON (J., 1925, 127, 1426) recently described the dibromide of 7-methoxy-3-homopiperonyl-2-methyl-1 : 4-benzopyrone (I), and showed that it was transformed by boiling with alcohol into a monobromo-substitution product of the original pyrone, which was formulated as the 6-bromohomopiperonyl derivative (II).



As some theoretical conclusions were drawn from this reaction, it has been considered advisable to establish definitely the constitution of the monobromo-derivative. The compound (II) has therefore been synthesised. It is identical in all respects with the product obtained from the dibromide, the original formula being thus confirmed.

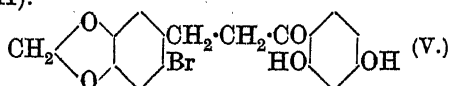
The synthesis was first attempted from 6-bromopiperonal by a series of reactions analogous to those used for the preparation of 7-methoxy-3-homopiperonyl-2-methyl-1 : 4-benzopyrone (Baker and Robinson, *loc. cit.*), but this was found impracticable. 6-Bromopiperonal could not be induced to condense with an alkaline, aqueous solution of sodium cyanoacetate, but it condensed readily with ethyl cyanoacetate in presence of piperidine, and the resulting ester was hydrolysed to 6-bromopiperonylidencyanoacetic acid (III). This



acid on reduction with sodium amalgam in aqueous solution gave, however,  $\alpha$ -cyano- $\beta$ -piperonylpropionic acid, the bromine atom being eliminated.

The nitrile (IV) was therefore prepared by bromination of  $\beta$ -piperonylpropionitrile, the position of the bromine atom being established by the fact that on hydrolysis it gave the corresponding acid, m. p. 139—140°, described by Weinstein (*Annalen*, 1885, 227, 43). The position of the bromine atom in Weinstein's acid was not known at the time, but it was prepared by the oxidation of the

acid  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , and its formation was accompanied by the production of a bromopiperonal, m. p.  $129^\circ$ , and a bromopiperonylic acid, m. p.  $204^\circ$ , both of which have since been shown to be 6-bromo-derivatives. It follows that the bromopiperonylpropionic acid was also the 6-derivative. By condensation with resorcinol under the conditions of the Hoesch synthesis  $\beta$ -6-bromopiperonylpropionitrile gave 6'-bromohomopiperonylresacetophenone (V), which by acetylation with acetic anhydride in presence of sodium acetate, followed by hydrolysis and methylation, gave the chromone (II).



### EXPERIMENTAL.

**6-Bromopiperonylideneacyanoacetic Acid (III).**—6-Bromopiperonal (10 g.), ethyl cyanoacetate (10 c.c.), alcohol (50 c.c.), and piperidine (10 drops) were heated for 10 minutes. The yellow crystals, m. p.  $131^\circ$ , obtained were identical with the product prepared by Bechert (*J. pr. Chem.*, 1894, 50, 19) by brominating piperonylideneacyanoacetic ester, which has since been shown by Piccinini (*Atti R. Accad. Sci. Torino*, 1905, 40, 463) to be the 6-bromo-derivative. By hydrolysis with a slight excess of alcoholic sodium hydroxide for 5 minutes, dilution, extraction with ether, and acidification, the acid was precipitated. It crystallised from much alcohol in bright yellow, lustrous needles, which melted on rapid heating at about  $300^\circ$  (decomp.) (Found: C, 44.7; H, 2.3; N, 4.9; Br, 27.1.  $\text{C}_{11}\text{H}_6\text{O}_4\text{NBr}$  requires C, 44.6; H, 2.0; N, 4.7; Br, 27.0%). It gives a yellow solution in concentrated sulphuric acid.

**$\beta$ -6-Bromopiperonylpropionitrile (IV).**—A mixture of  $\beta$ -piperonylpropionitrile (25 g.), glacial acetic acid (500 c.c.), and bromine (25 g.) was kept for  $\frac{1}{2}$  hour, heated for 5 minutes, and poured into water. The product crystallised from alcohol in colourless needles, m. p.  $81^\circ$  (Found: C, 47.4; H, 3.4; N, 5.7; Br, 31.8.  $\text{C}_{10}\text{H}_8\text{O}_2\text{NBr}$  requires C, 47.3; H, 3.2; N, 5.5; Br, 31.5%). The reaction mixture must not stand for longer, as owing to the action of hydrogen bromide and acetic acid  $\beta$ -6-bromopiperonylpropionamide separates. This crystallises from alcohol in colourless, lustrous needles, m. p.  $151^\circ$  (Found: C, 44.3; H, 3.9; N, 5.4; Br, 29.6.  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{NBr}$  requires C, 44.1; H, 3.7; N, 5.2; Br, 29.4%).  $\beta$ -6-Bromopiperonylpropionic acid crystallises from chloroform in colourless prisms, m. p.  $139$ – $140^\circ$  (Found: Br, 29.4. Calc., Br, 29.3%) (compare Weinstein, *loc. cit.*). In concentrated sulphuric acid, these substances, compound (V), and 6-bromopiperonal give cherry-red solutions, which

soon darken, turn brown, and finally brownish-green. In the last case, the final colour is more brown.

*6'-Bromohomopiperonylresacetophenone* (V).— $\beta$ -6-Bromopiperonyl-propionitrile (10 g.), resorcinol (20 g.), anhydrous ether (200 c.c.), and powdered zinc chloride (10 g.) were saturated with anhydrous hydrogen chloride, and again after 24 hours. After standing, the solid ketimine was washed with ether and hydrolysed by heating with water for 2 hours. The ketone was dissolved in aqueous sodium hydroxide, the solution extracted with ether, and the product precipitated by carbon dioxide (yield 4 g.). It crystallises from slightly diluted acetic acid in pale brown prisms, m. p.  $163^{\circ}$  (Found: C, 52.3; H, 3.5; Br, 21.6.  $C_{16}H_{13}O_5Br$  requires C, 52.6; H, 3.6; Br, 21.9%).

*7-Methoxy-3-(6'-bromohomopiperonyl)-2-methyl-1:4-benzopyrone* (II).—The above ketone (2 g.), anhydrous sodium acetate (2 g.), and acetic anhydride (20 c.c.) were heated at  $180^{\circ}$  for 36 hours. Treatment with water gave a dark, uncrystallisable oil, which was hydrolysed with dilute alcoholic sodium hydroxide. The phenolic compound was methylated at  $60^{\circ}$  with methyl sulphate and aqueous potassium hydroxide; a solid (1.4 g.) then separated which by crystallisation from alcohol (200 c.c.) (charcoal) formed bunches of pale brown prisms, m. p.  $206-207^{\circ}$ . The melting point was not depressed on admixture with a specimen of the bromo-derivative prepared from the dibromide (I). Further, its reaction with sulphuric acid was identical with that given by the compound prepared from (I). The cherry-red solution rapidly became somewhat purple and darker, then light grey, and finally bright olive-green, the changes occupying about 3 minutes at the ordinary temperature.

The author wishes to thank Professor R. Robinson for the interest he has taken in the research, and Mr. A. Pollard for assistance with a portion of the experimental work.

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### CXXXIX.—*Preparation and Resolution of dl-cis-2:5-Dimethylpiperazine.*

By FREDERIC BARRY KIPPING and WILLIAM JACKSON POPE.

ON reducing 2:5-dimethylpyrazine,  $N \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CH} \cdot \text{CMe} \end{smallmatrix} N$ , with sodium and alcohol, Stoehr (*J. pr. Chem.*, 1893, 47, 494; 1897, 55, 49) obtained two products which he described as the  $\alpha$ - and  $\beta$ -2:5-

dimethylpyperazines; the  $\alpha$ -compound constituted the main product and only small quantities of the  $\beta$ -isomeride were formed. Pope and Read identified Stoehr's  $\alpha$ -2 : 5-dimethylpyperazine as the *trans*-isomeride (J., 1912, **101**, 2325), but did not separate the  $\beta$ -compound from the reduction product of the pyrazine; they secured, however, a quantity of residues left during the manufacture of lycetol, the tartrate of the  $\alpha$ -base, and separated therefrom a substance which corresponded closely in properties with Stoehr's  $\beta$ -base. The study of the latter product (J., 1914, **105**, 219) conclusively proved it to be the *cis*-2 : 6-dimethylpyperazine, which Pope and Read hence supposed to be Stoehr's  $\beta$ -2 : 5-dimethylpyperazine. This supposition is now shown to be erroneous.

The confusion arose from the close similarity in physical properties between the *dl-cis*-2 : 5-dimethylpyperazine, m. p. 114—115°, and the *cis*-2 : 6-dimethylpyperazine, m. p. 110—111°; the 1 : 4-dibenzoyl derivatives melt at 145—146° and 147—148°, respectively, but mixtures of the two melt at about 120—130°.

The present paper describes the repetition of Stoehr's preparation of his  $\beta$ -2 : 5-dimethylpyperazine and the resolution of this compound into its *d*- and *l*-components. The resolution was effected by Pope and Read's method of condensation with *d*-hydroxymethylenecampbor, and Stoehr's  $\beta$ -compound is thus proved to be the *dl-cis*-2 : 5-dimethylpyperazine.

#### EXPERIMENTAL.

*iso*Nitrosoacetone (270 g.) was prepared from ethyl acetoacetate (700 g.) by the method of Ceresole (*Ber.*, 1882, **15**, 1326) and then reduced by the method of Gabriel and Pinkus (*Ber.*, 1893, **26**, 2206) to 2 : 5-dimethylpyrazine, each 50 g. yielding about 12 g. of the base. The 2 : 5-dimethylpyrazine (10 g.) was then reduced as described by Stoehr and the mixture of  $\alpha$ - and  $\beta$ -dimethylpyperazine hydrochlorides (about 8 g.) isolated; the operation was repeated until about 160 g. of the salt had been obtained. The dried and powdered hydrochloride was repeatedly extracted with boiling absolute alcohol, in which the  $\alpha$ - or *trans*-compound is very sparingly soluble; the alcoholic extract on evaporation yielded about 8 g. of crude *dl-cis*-dimethylpyperazine. The reduction product of the pyrazine thus contains about 95% of the *trans*-compound and only about 5% of the *cis*-isomeride.

*dl*-1 : 4-Dibenzoyl-*cis*-2 : 5-dimethylpyperazine.—This compound, prepared by the Schotten-Baumann reaction from the hydrochloride, crystallises from alcohol in colourless prisms, m. p. 145—146°; Stoehr gives 147—148° for his  $\beta$ -compound. Analysis failed to reveal the presence of a molecule of water of crystallis-

ation indicated by Stoehr (Found: C, 74.4; H, 6.8; N, 8.7. Calc. for  $C_{20}H_{22}O_2N_2$ , C, 74.5; H, 6.8; N, 8.7%); the identity in composition between the  $\alpha$ - and  $\beta$ -compounds may be associated with the close similarity in crystalline form previously noted (J., 1914, 105, 223). As remarked above, the compound depresses the melting point, namely, 145–146°, of Pope and Read's 1:4-dibenzoyl-*cis*-2:6-dimethylpiperazine.

*The p-Toluenesulphonyl Derivatives.*—In view of the similarity in melting point between the *cis*-2:5- and *cis*-2:6-isomerides just noted, it was thought desirable to prepare other acidic derivatives. The 1:4-di-*p*-toluenesulphonyldimethylpiperazines were made by warming the hydrochlorides of the base with *p*-toluenesulphonyl chloride and caustic soda solution.

1:4-Di-*p*-toluenesulphonyl-*cis*-2:5-dimethylpiperazine crystallises from alcohol in minute, colourless prisms, m. p. 146–147°, the melting point being the same as that of the corresponding benzoyl derivative (Found: C, 56.9; H, 6.15.  $C_{20}H_{16}O_4N_2S_2$  requires C, 56.8; H, 6.2%).

1:4-Di-*p*-toluenesulphonyl-*trans*-2:5-dimethylpiperazine is almost insoluble in the usual solvents and after washing with alcohol melted at 225°; it is remarkable that this melting point is also identical with that of the benzoyl derivative (Found: C, 56.9; H, 6.2%).

1:4-Di-*p*-toluenesulphonyl-*cis*-2:6-dimethylpiperazine is very soluble in alcohol and acetone, but less soluble in light petroleum; it crystallises from the latter, to which a little alcohol has been added, in needles, m. p. 89–90° (Found: C, 56.8; H, 6.2%). The marked difference in physical properties between these three isomerides is further confirmation of the separate identity of the three parent bases.

*Resolution of cis-2:5-Dimethylpiperazine.*—The hydrochloride of the racemic base was boiled in alcoholic solution with caustic potash (2 mols.) and *d*-hydroxymethylenecamphor (2 mols.) for  $\frac{1}{2}$  hour; the gummy deposit obtained on pouring into water crystallised on treatment with light petroleum and then melted at 167–170°. On fractional crystallisation from light petroleum containing a little alcohol *d*-*cis*-2:5-dimethylpiperazine-*d*-bismethylenecamphor,  $C_8H_{14} \begin{array}{c} \diagup C:CH \cdot N-CH_2-CHMe \diagdown \\ CO \quad CHMe-CH_2-N-CH=C \end{array} OC \begin{array}{c} \diagup \\ \diagdown \end{array} C_8H_{14}$ , was obtained in colourless needles, m. p. 210°. 0.1016 G. made up to 20 c.c. with alcohol gave  $\alpha_{5461} + 7.6^\circ$  in a 2-dcm. tube; whence  $[\alpha]_{5461}^{20} = +747^\circ$ . The more soluble fraction after several crystallisations melted at 176–177°; this product represents 1-*cis*-2:5-dimethylpiperazine-*d*-bismethylenecamphor which still contained some stereo-

isomeride and gave  $[\alpha]_{5461}^{20} + 635^{\circ}$  in alcoholic solution (Found: C, 76.8; H, 9.6.  $C_{28}H_{42}O_2N_2$  requires C, 76.7; H, 9.6%).

The *d*- and *l*-dimethylpiperazines were separated from the above derivatives by treatment with bromine by the method of Read and Pope and isolated as the hydrobromides; neither salt showed measurable rotatory power in alcoholic solution. In many analogous cases, however, the specific rotation of a base is a small fraction of that of the benzoyl derivative; the *d*- and *l*-hydrobromides were therefore benzoylated in the hope that optical activity might be detected.

*d*- and *l*-1:4-Dibenzoyl-*cis-2:5-dimethylpiperazine*.—The *d*-isomeride was obtained pure by crystallisation from acetone and forms colourless prisms, m. p. 164–165° (Found: C, 75.1; H, 6.7.  $C_{20}H_{22}O_2N_2$  requires C, 74.5; H, 6.8%). 0.0985 G. made up to 20 c.c. with alcohol gave  $\alpha_{5461} + 2.44^{\circ}$  in a 2-dcm. tube; whence  $[\alpha]_{5461} = + 247^{\circ}$ .

The *l*-isomeride was not separable in a pure state from the material available, and the best specimen obtained melted at 140–142° and gave  $[\alpha]_{5461} - 146^{\circ}$  in alcoholic solution.

In order to make sure that these compounds had not been confused with the benzoyl ester of hydroxymethylenecamphor, which has nearly the same carbon and hydrogen content, the latter substance was prepared; it melts at 119–120° (Bishop, Claisen, and Sinclair, *Annalen*, 1894, 281, 374). 0.0820 G. made up to 20 c.c. with alcohol gave  $\alpha_{5461} + 1.44^{\circ}$  in a 2-dcm. tube, whence  $[\alpha]_{5461}^{20} = + 175^{\circ}$ . Further to ensure that no confusion has occurred, the *trans-2:5-dimethylpiperazine-d*-methylenecamphor of Pope and Read (J., 1912, 101, 2334) was again recovered from the various fractions and converted into its benzoyl derivative. In no case was an optically active benzoyl derivative obtained.

### Summary.

Stoehr's  $\beta$ -2:5-dimethylpiperazine has been identified as the *cis*-isomeride by resolving it into optically active components. It is not identical with the *cis-2:6-dimethylpiperazine* of Pope and Read, although the similarity in physical properties between the two bases and their corresponding derivatives is such as to suggest identity.

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CXL.—*Interactions of Tellurium Tetrachloride and Aryl Alkyl Ethers. Part II.*

By GILBERT T. MORGAN and RICHARD EATOUGH KELLETT.

THE interaction of tellurium tetrachloride and anisole is first mentioned in a communication by Michaelis (*Ber.*, 1897, 30, 2821) on organic compounds containing inorganic radicals, where he refers to the ready introduction of the bivalent radicals  $\text{SeCl}_2$  and  $\text{TeCl}_2$  into various classes of organic substances. Aromatic derivatives of the former radical had been previously described by one of his pupils, Kunckell (*Ber.*, 1895, 28, 609), and Michaelis was then announcing the discovery of an analogous series of tellurium derivatives, the work of Rust, another collaborator in the Rostock laboratories (*Ber.*, 1897, 30, 2828).

By warming together tellurium tetrachloride (1 mol.) and anisole (2 mols.), Rust obtained a yellow compound to which, from his analyses given in duplicate, he gave the name "dichlorotelluro-anisol" with formula  $\text{TeCl}_2(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$ . This substance was purified from crude material by transforming the latter into dihydroxide,  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{Te}(\text{OH})_2$ , and regenerating the dichloride with hydrogen chloride.

From this dihydroxide Rust also prepared the dibromide,  $\text{TeBr}_2(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$ , di-iodide,  $\text{TeI}_2(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$ , dinitrate,  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{Te}(\text{NO}_3)_2$ , and chloroplatinate,  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2\cdot\text{PtCl}_4$ .

The subject was next taken up by Rohrbach (*Annalen*, 1901, 315, 9), who referred to the dissimilarities observable in the behaviour of selenium tetrachloride and tellurium tetrachloride as regards their condensations with aryl alkyl ethers. In the former case two substances were obtained, bisanisyl selenide and bisanisyl selenidichloride, whereas in Rust's experiments bisanisyl telluridichloride was the sole product.

In order, therefore, to obtain bisanisyl telluride, Rohrbach removed chlorine from Rust's alleged dichloride with zinc dust in benzene and obtained a highly coloured compound which he stated was "*p*-telluroanisole,"  $\text{Te}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$ . He also converted this alleged monotelluride, by suitable treatment with chlorine, bromine, and dilute nitric acid, respectively, into Rust's dichloride, dibromide and dinitrate.

Fourteen years later, Rohrbach's supposed bis-*p*-anisyl telluride,  $\text{Te}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$ , was examined by Lederer (*Ber.*, 1915, 48, 1424), who prepared its mercurichloride, mercuribromide, and mercuriodide,  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{TeHgX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ). Lederer also obtained

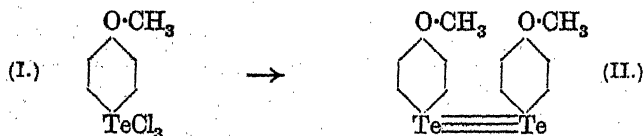


(*loc cit.*, p. 2053) by the action of methyl iodide on Rohrbach's telluride a product yielding anisoledimethyltelluronium picrate. But the conclusions which he drew from this methylation have, however, been already shown to be groundless and a complete explanation of the reaction has been given in the previous paper on this subject (Morgan and Drew, J., 1925, 127, 2310).

In a subsequent paper, Lederer (*Ber.*, 1916; 49, 1076) obtained the true bis-*p*-anisyl telluride by the interaction of tellurium dibromide and magnesium *p*-anisyl bromide and converted this telluride into dichloride, dibromide, di-iodide, and oxide. The whole para-series differed essentially from the corresponding derivatives of Rohrbach's telluride made either by that investigator, or by Rust or by Lederer himself. Later, Lederer prepared the corresponding members of the meta- and ortho-series, again using the Grignard reaction but with the appropriate magnesium *m*- or *o*-anisyl iodide (*Ber.*, 1919, 52, 1989; 1920, 53, 712), and since these two series also differed from Rohrbach's presumably isomeric series it followed by exclusion that, in the Rust-Rohrbach preparations, tellurium had been introduced into the side chain, thus giving the formula  $\text{Br}_2\text{Te}(\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_5)_2$ . But this conclusion is fallacious, because the original assumption of isomeric relationship between the Rust-Rohrbach and Lederer series of compounds is incorrect.

The researches described in the present communication furnish a correct explanation of the foregoing differences.

The compound first handled by Rust was not dichlorotelluro-bisanirole,  $\text{Cl}_2\text{Te}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$ , but *p*-anisyltelluritrichloride (I), and accordingly its highly coloured reduction product obtained by Rohrbach with complete elimination of chlorine was not a bisanisyl telluride  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_5-\text{H})_2\text{Te}$ , but bis-*p*-anisyl ditelluride (II).



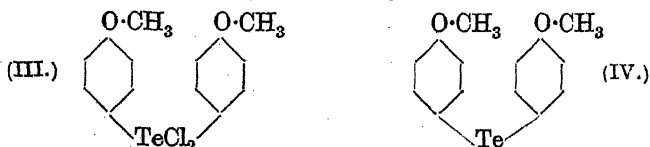
Hence Lederer's discussion of the constitution of Rohrbach's assumed bisanisyl telluride is irrelevant, inasmuch as he was not even dealing with an isomeride of his three *o*-, *m*-, and *p*-bisanisyl tellurides.

Our experiments show conclusively that *p*-anisyltelluritrichloride (I) is the sole product of the interaction of tellurium tetrachloride (1 mol.) and anisole (3 mols.) in warm chloroform, the yield being quantitative. In the preparations made by Rust and by Lederer the reagents were heated together without solvent on the water-bath, but on repeating their experimental conditions we again

obtained *p*-anisyltelluritrichloride as the sole product. The yellow colour of the substance and its mode of hydrolysis together with complete analytical data confirm our conclusions as to its constitution (I).

On reduction with potassium metabisulphite, the trichloride gave a quantitative yield of bis-*p*-anisyl ditelluride (II), obtained in dark brownish-red crystals with green, metallic lustre. In its intense colour this ditelluride resembles Lederer's bisphenyl ditelluride (*Ber.*, 1915, 48, 1345), which is described as separating in blood-red crystals. Further evidence for the composition of bis-*p*-anisyl ditelluride (II) is afforded by molecular-weight determination and by the large tellurium content of the compound.

It now remained to prepare the true *bis-p-anisyltelluridichloride* (III) and this was accomplished by heating tellurium tetrachloride with excess of anisole at 150–180°; this dichloride was then obtained in practically quantitative yield.



This dichloride (III), unlike the trichloride (I), is colourless and reducible only with difficulty, but when the chlorine is removed entirely with zinc dust, the product, *bis-p-anisyl telluride* (IV), is also colourless. As already pointed out in earlier papers on organic tellurium compounds, these colour differences are themselves a useful guide to the constitution of tellurium derivatives (Morgan and Drew, J., 1925, 127, 531, 2307).

Having thus established the nature of the tellurium anisyl derivatives, we made comparative experiments on the next homologues of anisole and found that the formation of telluritrichlorides took place most readily with *o*-tolyl methyl ether, and the resulting yellow 2-methoxytolyl-5-telluritrichloride was reducible to the intensely coloured bis-2-methoxy-5-tolyl ditelluride. Telluritrichlorides were obtained, but with greater difficulty, from *m*- and *p*-tolyl methyl ethers.

*Addendum. Interaction of Tellurium Tetrachloride and the Homologues of Acetic Anhydride.*

During this collaboration, experiments were also made to ascertain whether the condensation found to take place between tellurium tetrachloride and acetic anhydride (Morgan and Drew, J., 1925, 127, 531) could be effected with anhydrides of the homologues of acetic acid.

The results showed that the tendency to undergo this condensation with tellurium tetrachloride fades away rapidly as the homologous series is ascended.

*Trichlorotelluripropionic acid* obtained from propionic anhydride was reducible to *ditellurodipropionic acid*. With *n*-butyric anhydride, tarry products predominated and only a very little of the telluriferous butyric acid was observed. With *isovaleric* anhydride, a considerable proportion of the tetrachloride was reduced with elimination of tellurium.

## EXPERIMENTAL.

### *Condensation of Tellurium Tetrachloride and Anisole.*

1. *Interaction in Chloroform*.—Tellurium tetrachloride (2 g.), 2.4 g. of anisole, and 30 c.c. of dry chloroform were heated on the water-bath for 2 hours. The mixture became yellowish-red even in the cold, but on warming hydrogen chloride was evolved copiously and the condensation product crystallised to a mass of yellow needles. No tellurium was evolved and the condensation proceeded quantitatively. The crude product melted at 190° and gave Cl, 30.7% (Calc. for di- and tri- chlorides, Cl, 17.2 and 31.2, respectively).

In contact with water, this crude yellow trichloride was hydrolysed to a white hydroxide. When treated with cold aqueous potassium metabisulphite ( $2\frac{1}{2}$  mols.), the hydroxide was reduced to an insoluble dark red product which on crystallisation from dilute alcohol melted at 57° and gave Te, 56.8% (Calc. for dianisyl monotelluride and ditelluride, Te, 37.3 and 54.8 respectively).

The foregoing analyses, even when effected on the crude products of reaction, show that in chloroform, tellurium tetrachloride and anisole (3 mols.) yield an anisyltelluritrichloride which on reduction furnishes dianisyl ditelluride.

2. *Condensation without Solvent* (Method of Rust and Lederer).—The trichloride obtained by the foregoing procedure was apparently identical with Rust's "dichlorotelluroanisole," although our analysis indicated a trichloride. As the solvent used in our experiments may have modified the reaction, we repeated the condensation according to Rust's recipe, which is practically identical with the method adopted by Lederer (*loc. cit.*). The crude products in two preparations melted at 195° and 190° and after one crystallisation from dry chloroform gave Cl, 29.8 and 30.9%, whereas the di- and tri-chlorides require, respectively, Cl, 17.2 and 31.2%.

Reduction of the foregoing products of the dry process with ice-cold aqueous potassium metabisulphite furnished a substance which crystallised from warm alcohol, on addition of water, in dark red,

glistening crystals, m. p. 57°. Reduction with zinc dust in benzene led to a dark red oil, the alcoholic solution of which yielded a dark red substance melting at 49–51°, a melting point corresponding with Rohrbach's 50° and Lederer's "50° not easily observed because of the dark colour."

*p*-Anisyltelluritrichloride,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{TeCl}_3$ .—On warming together tellurium tetrachloride (1 mol.) and anisole ( $1\frac{1}{2}$ –2 mols.) in dry chloroform solution a practically quantitative yield of the trichloride was obtained, calculated on the tetrachloride; the product separated directly in a nearly pure condition. Dry chloroform or ether was used for recrystallisation, the substance separating in yellow needles, m. p. 190° (Found: C, 24.3, 24.7; H, 2.3, 2.1; Cl, 31.1; Te, 37.7.  $\text{C}_7\text{H}_7\text{OCl}_3\text{Te}$  requires C, 24.6; H, 2.05; Cl, 31.2; Te, 37.4%).\*

*p*-Anisyltelluritrichloride was almost insoluble in cold chloroform, benzene, or light petroleum and dissolved only moderately in the warm solvents. With water and moist solvents, it decomposed to a white hydroxide; it dissolved completely in hydrochloric acid or aqueous caustic soda.

Acetic acid added to a solution of 2 g. of *p*-anisyltelluritrichloride in 2*N*-sodium hydroxide precipitated a white amorphous powder having no definite melting point. Dissolution in alkali and precipitation with acetic acid were repeated; the amorphous product, after drying, gave C, 28.4; H, 2.6; whereas a trihydroxide,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Te}(\text{OH})_3$ , would require C, 29.4; H, 3.5%. As the substance was insoluble in ordinary solvents and uncrystallisable, it was not investigated further. For a product obtained under essentially the same conditions Rust obtained Te, 33.55, 33.60; C, 44.37, 44.46; H, 4.34, 4.33%, corresponding with a di-*p*-anisyltelluridihydroxide,  $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{Te}(\text{OH})_2$ . Two other carbon and hydrogen determinations confirmed the lower values for these elements, and a portion of the hydroxide when evaporated with concentrated hydrochloric acid regenerated yellow needles of *p*-anisyltelluritrichloride (m. p. 191°. Found: Cl, 30.3; calc., Cl, 31.2%).

This hydrated oxide dissolved in warm dilute nitric acid and, on cooling, a yellowish-pink, amorphous precipitate separated (m. p. 190–210°); the filtrate yielded yellowish-white plates, identified by melting point and analysis as 2:4-dinitrophenol.

*Bis-p-anisyltelluride* (II), obtained in almost quantitative yield

\* Tellurium is most satisfactorily determined in these compounds by the Carius method (9–10 hours at 260°); the solution is evaporated to dryness with hydrochloric acid, the residue dissolved in water, and the tellurium precipitated with hydrazine hydrochloride and sulphurous acid.

on adding gradually potassium metabisulphite to *p*-anisyltelluritrichloride suspended in ice-water, crystallised from dilute alcohol or petroleum (b. p. 40–60°) in reddish-brown crystals. From its more concentrated solution in benzene the ditelluride separated in highly lustrous, green crystals (Found: C, 35.6; H, 3.0; Te, 54.2; *M*, cryoscopic in benzene, 472.5.  $C_7H_7OTe$  requires C, 35.8; H, 3.0; Te, 54.4%.  $C_{14}H_{14}O_2Te_2$  requires *M*, 469).

The ditelluride oxidised slowly in air to a yellowish-grey substance, and its alcoholic solution was at once decolorised by hydrogen peroxide; a white, amorphous product was obtained on concentrating the liquid. On passing chlorine through its chloroform solution, the colour changed and *p*-anisyltelluritrichloride crystallised out (m. p. 192°). Bromine in similar circumstances yielded *p*-anisyltelluritribromide, separating in orange-yellow crystals, m. p. 187.5° (Rust's dibromotelluroanisole melted at 183–185°). This tribromide was hydrolysed by water to the white hydroxide and with metabisulphite it regenerated the di-*p*-anisyl ditelluride. On adding aqueous mercuric chloride to the ditelluride in ethereal solution, a light brown mercurichloride was precipitated.

*Di-p-anisyltelluridichloride* (III).—Tellurium tetrachloride (15 g.) and 30 g. of anisole (5 mols.) were heated for 24 hours at 150–180°, the solution being afterwards allowed to solidify in a vacuum. The yield of crystalline product was 95% of the theoretical. The dichloride crystallised from benzene-petroleum (b. p. 40–60°) in colourless prisms, often retaining a slightly pink tinge; it melts at 181–182° (Found: C, 40.5; H, 3.6; Cl, 17.25; Te, 30.9.  $C_{14}H_{14}O_2Cl_2Te$  requires C, 40.7; H, 3.4; Cl, 17.2; Te, 30.9%). The dichloride was insoluble in water, although slightly hydrolysed by this solvent; it was completely hydrolysed by aqueous sodium hydroxide, but dissolved only sparingly in excess of this alkali. It was not readily reduced, being resistant to the action of metabisulphite and only attacked with difficulty by zinc dust.

*Bis-p-anisyl Telluride* (IV).—Di-*p*-anisyltelluridichloride (10 g.) and 5 g. of zinc dust in 150 c.c. of benzene were heated for 24 hours under reflux. Some tar separated and the filtered solution was concentrated. The white crystals which separated still contained chlorine and were subjected to the action of more zinc dust until all the halogen was eliminated. The halogen-free compound (yield 37%) crystallised from dilute alcohol in colourless, nacreous plates, m. p. 53–54° (Found: C, 49.0; H, 4.2; Te, 37.6.  $C_{14}H_{14}O_2Te$  requires C, 49.2; H, 4.1; Te, 37.3%).

On mixing chloroform solutions of the telluride and bromine, di-*p*-anisyltelluridibromide separated in sulphur-yellow crystals,

m. p. 190°; the bromo-derivative of Rohrbach's ditelluride was described as orange-yellow.

*2-Methoxytolyl-5-telluritrichloride*,  $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{CH}_3)\cdot\text{TeCl}_3$ .—Four g. of tellurium tetrachloride (1 mol.) and 3.7 g. of *o*-tolyl methyl ether (2 mols.) in 30 c.c. of dry chloroform were heated together on the water-bath; hydrogen chloride was evolved and, after one hour, yellow needles separated (Found: Cl, 29.6.  $\text{C}_8\text{H}_5\text{OCl}_3\text{Te}$  requires Cl, 30.0%). The product was only very sparingly soluble in ordinary organic media with the exception of acetone, but when separating from this solvent after the addition of light petroleum, the crystals obtained were progressively whiter and showed a diminution in the percentage of chlorine.

These decomposition products were extracted with chloroform and the filtered solution was saturated with hydrogen chloride. A deposit of pale yellow needles was formed melting to a red liquid at 232–233° (Found: Cl, 30.0%).

The trichloride was insoluble in cold water, but hydrolysed, on warming, to a white hydroxide which dissolved readily in benzene or chloroform. With potassium metabisulphite, the trichloride was reduced to a highly coloured ditelluride.

A large excess of *o*-tolyl methyl ether and tellurium tetrachloride with a little dry chloroform were gradually heated to 170°; the solid product was filtered from unchanged ether and extracted under reflux with chloroform, but no soluble dichloride was obtained.

*Bis-2-methoxy-m-tolyl Ditelluride*,  $\{\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{CH}_3)\cdot\text{Te}\}_2$ .—To 5 g. of the preceding trichloride in 50 c.c. of ice-cold water were added slowly 9.5 g. of potassium metabisulphite (3 mols.); the reduction proceeded rather more slowly than in the case of the anisyl derivative, the colour changing from yellow to black. After stirring occasionally for an hour, the black residue was extracted with ether. The dark red solution deposited dark needles, which recrystallised from petroleum (b. p. 40–60°) in similar forms with a brownish-green bronzy lustre; m. p. 77–78° (Found: C, 38.6; H, 3.6; Te, 51.5; *M*, cryoscopic in benzene, 493.  $\text{C}_8\text{H}_5\text{OTe}$  requires C, 38.6; H, 3.6; Te, 51.3%.  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Te}_2$  requires *M*, 497).

This ditelluride was very soluble in benzene, chloroform, acetone or ether, but only sparingly soluble in cold alcohol or petroleum (b. p. 40–60°), dissolving more readily on warming. From its alcoholic solution, water precipitated a bright red emulsion which solidified to a dark green, crystalline mass. Hydrogen peroxide instantly decolorised the alcoholic solution. Chlorine passed into the chloroform solution regenerated 2-methoxytolyl-5-telluritrichloride; bromine under similar conditions combined additively to form the corresponding orange-yellow tribromide.

*4-Methoxytolyl-3-telluritrichloride.*—*p*-Tolyl methyl ether and tellurium tetrachloride did not interact appreciably in chloroform solution, but at higher temperatures condensation took place. Equal parts of the tetrachloride and *p*-tolyl ether with a trace of chloroform were heated on the water-bath until hydrogen chloride was no longer evolved. The resulting yellow liquid slowly yielded greenish-yellow crystals, which underwent partial hydrolysis in such solvents as moist benzene, chloroform and acetone. Accordingly these products were redissolved in dry chloroform and the pale yellow solution was saturated with hydrogen chloride. On concentrating the liquid in a vacuum desiccator, well-defined, yellow, rectangular plates separated, m. p. 135° (Found: Cl, 29.6.  $C_8H_9OCl_3Te$  requires Cl, 30.0%). The reduction of this and the following trichloride proceeded less readily than that of their foregoing isomeride.

*3-Methoxytolyl-(4 or 6)-telluritrichloride.*—Equal parts of tellurium tetrachloride and *m*-tolyl methyl ether with a little chloroform were heated on the water-bath until evolution of hydrogen chloride had ceased; the oily residue was then cooled until dark green crystals separated. When the crude material was dissolved in dry chloroform and the solution saturated with hydrogen chloride, no precipitation occurred, but slow evaporation in a vacuum desiccator furnished a yellowish-brown crystalline mass, m. p. 154° (Found: Cl, 28.2. Calc., Cl, 30.0%). This trichloride is much more soluble than its isomeride in organic media, but exposure to moisture leads to considerable hydrolysis.

Condensation between tellurium tetrachloride and each of the following:  $\beta$ -naphthyl methyl ether, monoethyl ethers of resorcinol and quinol, monomethyl ether of quinol, led to viscid, uncrystallisable products. No appreciable interaction was observed with *p*-nitroanisole, but a preliminary experiment with *p*-bromoanisole indicated a normal condensation to a *trichloride*, m. p. 184°; this was reducible by aqueous metabisulphite to a dark red oily ditelluride, which was brominated in chloroform solution to an orange-yellow *tribromide*, m. p. 153°.

*Interaction of Tellurium Tetrachloride and the Homologues of Acetic Anhydride.*

*Trichlorotelluripropionic Acid*,  $Cl_3Te \cdot CH(CH_3) \cdot CO_2H$ . Five g. of tellurium tetrachloride and 7 g. of propionic anhydride (3 mols.) in 38 c.c. of chloroform were heated under reflux for 4 hours. Hydrogen chloride was evolved slowly, and 0.3 g. of tellurium eliminated. The filtered liquid was concentrated in a vacuum desiccator, and chloroform added; a brown solid then separated (yield 4 g.). The product was extremely soluble in all organic

media and could not be freed by recrystallisation from tarry impurities. A halogen estimation on the crude material, obtained in white plates by allowing the viscous liquid from the foregoing condensation to remain in a vacuum desiccator for 4 weeks, gave Cl, 34.7 ( $\text{C}_3\text{H}_5\text{O}_2\text{Cl}_3\text{Te}$  requires Cl, 34.6%). This substance melted at 145–150° and on exposure to the atmosphere the crystals became liquid. A condensation with a large excess (6 mols.) of propionic anhydride gave a smaller yield of the trichloro-compound.

*Ditellurodipropionic Acid*,  $\{\text{Te}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{H}\}_2$ .—Crude trichlorotelluripropionic acid was reduced with aqueous metabisulphite (2.5 mols.), and the yellow solution extracted with ether. The oily residue from the ethereal extract redissolved in chloroform to a solution which yielded a brick-red solid, m. p. 75°. The pale yellow *silver* salt was photosensitive and became brownish-black on exposure, the *copper* salt was a pale green precipitate decomposing at 175°, the soluble *potassium* salt separated from concentrated aqueous solution in brick-red plates blackening at 175°.

*Tribromotelluripropionic Acid*,  $\text{Br}_3\text{Te}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}_2\text{H}$ , resulted from the interaction of ditellurodipropionic acid and bromine in chloroform; it separated as a yellow oil which solidified to a bright yellow solid, m. p. 139–141° (Found: Br, 53.8.  $\text{C}_3\text{H}_5\text{O}_2\text{Br}_3\text{Te}$  requires Br, 54.4%). This tribromo-derivative dissolved readily in ether or acetone or in warm benzene, chloroform or ethyl acetate, separating from these solutions, on addition of light petroleum, as an oil which slowly solidified. When kept in a sealed tube, the yellow tribromo-compound changed into a greenish-black decomposition product.

Tellurium tetrachloride and *n*-butyric anhydride when boiled in chloroform solution slowly evolved hydrogen chloride, but the tarry product as extracted with acetone and other organic solvents remained oily. The acidic nature of this product was demonstrated by the formation of a yellow *silver* and green *copper* salt. Bromine in chloroform gave an oily additive product. Interaction between tellurium tetrachloride and isovaleric anhydride was attended by elimination of a considerable proportion of tellurium. From an experiment with monochloroacetic anhydride, the greater part of the tellurium tetrachloride was recovered.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the Research Committee of the University of Birmingham for grants which have helped to defray the expense of this investigation.

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CXLI.—*The Behaviour of Mannose Diacetone on Methylation.*

By JAMES COLQUHOUN IRVINE and ANDREW FORRESTER SKINNER.

IN the course of a discussion on the application of the methylation process to the structural problems of carbohydrates, it was stated (Irvine and Oldham, J., 1925, 127, 2910) that the method is valid only if certain conditions are fulfilled. These need not be enumerated again, but obviously the fundamental requirement is that during alkylation methyl groups are introduced into the vacant hydroxyl positions without disturbing any substituting groups already present. Equally important is the condition that, once methyl groups have entered the non-glucosidic positions of a sugar chain, they should remain unaffected during the standard processes employed to hydrolyse glucosides, disaccharides or polysaccharides. So far, no authentic case has been encountered which indicates that the above primary conditions are not fulfilled. One apparent exception was, however, recorded by Freudenberg and Hixon (*Ber.*, 1923, 56, 2119), who converted mannose diacetone into a monomethyl derivative and subjected the product to mild hydrolysis in the hope that monomethyl mannose would be formed. Contrary to expectation, not only the unstable isopropylidene residues were removed, but the methyl group also was eliminated so that the final product consisted of mannose. The subject was reinvestigated by Levene and Meyer (*J. Biol. Chem.*, 1924, 59, 145), who varied the procedure by applying the silver oxide method of alkylation to mannose diacetone, but the monomethyl derivative obtained, whilst differing in optical activity from Freudenberg's product, displayed precisely the same instability towards acid hydrolysts.

These observations, although capable of simple explanation, have elicited some criticism of the principles underlying the researches associated with this laboratory, and it is advisable to clear up the situation. It was assumed, prematurely, that, as mannose diacetone has no effect on Fehling's solution, the reducing position of the parent sugar had been substituted by a ketonic residue. In such an event, one hydroxyl group should persist in the sugar chain and undergo methylation, giving, irrespective of the method employed, the same monomethyl derivative. This product, in turn, when treated with aqueous acid should give a reducing sugar, *viz.*, monomethyl mannose. Two views have been put forward to account for the fact that the methyl group is removed on hydrolysis, the first being that the stability of methylated sugars is not a general feature of these compound and is considerably less than our published papers

indicate. Alternatively, it has been suggested that, in the particular case under consideration, the entry of a methyl group had dislodged a ketonic residue from its initial attachment to the reducing position and, through subsequent rearrangement, had formed a derivative differing in type from the parent compound.

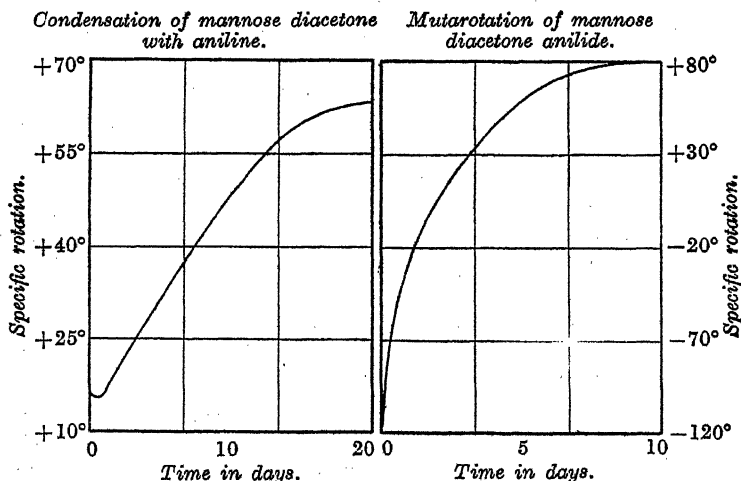
Either of the above explanations, if supported by convincing experimental evidence, would be damaging to the fundamental ideas underlying much of our work, but the suggestions are both highly improbable and opposed to experience. To the worker familiar with the properties of methylated sugars and glucosides, the apparently irregular behaviour of monomethyl mannose diacetone presents no difficulties whatsoever. The properties of the compound clearly show that it is *γ-methylmannoside diacetone*, and this could be formed only if mannose diacetone contained a labile hydrogen atom in the 1-position. That such is the case is shown by the fact that the compound forms a sodium derivative convertible into a monomethyl ether showing  $[\alpha]_D - 41^\circ$  in acetylene tetrachloride, whereas when methylation is effected directly by the silver oxide reaction the specific rotation of the product is widely different ( $[\alpha]_D + 23^\circ$ ). This is but an example of the general rule that when a reducing sugar is acted on by silver oxide and methyl iodide two stereoisomeric glucosides are produced, the  $\beta$ -variety being formed in excess. It follows that the monomethyl mannose diacetone obtained respectively by Freudenberg and by Levene differed merely in the relative proportions of two stereoisomeric substituted methylmannosides. From such compounds, again following a general rule, the alkyl group should be removed, as was the case, by hydrolysis. The only apparent irregularity is the extreme ease with which this group is lost, but even this feature is diagnostic and the explanation was already available. It has been known for a considerable time that  $\gamma$ -glucosides undergo hydrolysis with a facility comparable with that displayed by sucrose, and more recently (Irvine and Burt, J., 1924, 125, 1343)  $\gamma$ -methylmannoside has been shown to possess the same instability. Any confusion which may have arisen through the behaviour of mannose diacetone on methylation is due to attaching more importance to a single test, viz., the action of Fehling's solution, than to the numerous and more regular reactions of methylated sugars generally. Without additional experimental work it was possible to predict that mannose diacetone would (1) display mutarotation, (2) form the corresponding methylmannoside by the action of acid methyl alcohol, (3) undergo oxidation and reduction without removal of the acetone residues, and (4) condense with amino-bases.

In the interests of our general research programme we decided to

explore the case, but meanwhile Freudenberg has extended his work and has shown that mannose diacetone exhibits mutarotation and enters into condensation with ammonia (Freudenberg and Wolf, *Ber.*, 1925, 58, 300). More recently, Ohle and Berend (*ibid.*, p. 2950) have succeeded in oxidising mannose diacetone to a substituted mannonic acid, in which the ketonic residues persist, thus adding to the evidence that in the parent compound the reducing group is free. As our additional results are conclusive, and incidentally, have a bearing on the constitution of mannose diacetone, they are now submitted.

We have subjected mannose diacetone to the action of methyl alcohol containing 0.1% of hydrogen chloride, a methylating reagent

FIG. 1.



which is selective in the case of sugars, as it affects only the reducing position. Condensation proceeded readily and the optical changes involved, which are quoted in the experimental part, reveal that the substituted methylmannoside formed belongs to the  $\gamma$ -series. As anticipated, methylation proceeded without removing the acetone residues and the product was completely hydrolysed with the same facility as a  $\gamma$ -mannoside. Evidence was also obtained that mannose diacetone forms a phenylhydrazone, but as the product was a syrup and as, in the mannose series, aniline is a superior reagent to phenylhydrazine, the anilide was studied in greater detail. Mannose diacetone reacts in the cold with an alcoholic solution of aniline to give a well-defined crystalline *mannose diacetone anilide*. The polarimetric curve illustrating the change shows that two simulta-

eous reactions are involved and, following the general rule, the anilide displayed extensive mutarotation in alcoholic solution.

It will be observed that whereas during anilide formation the activity increases in the dextro-sense the compound when isolated is *laevorotatory*. In the preparation of mannoseanilide a similar anomaly is encountered.

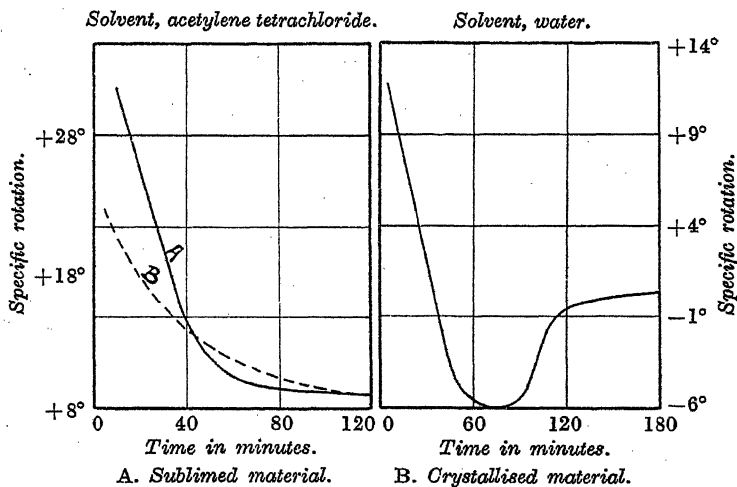
The mutarotation of mannose diacetone in various solvents has also been studied, the observations being made on material which had been repeatedly crystallised, or preferably, sublimed at  $120^{\circ}/0.2$  mm. A number of interesting features were encountered, particularly in the case of aqueous solutions where the phenomenon is abnormal and is probably more correctly described as "pseudo-mutarotation." Using dry acetone as the solvent, the mutarotation remained suspended and consequently the initial value ( $[\alpha]_D + 38.4^{\circ}$ ) may be taken as a standard for the compound. The reaction was, however, catalysed by the addition of a trace\* of *N*/50-sodium hydroxide, the constant value  $+ 16.9^{\circ}$  being reached in 6 hours. A solution in acetylene tetrachloride showed practically the same range, but gave the initial specific rotation  $[\alpha]_D + 31.5^{\circ}$ , which diminished regularly to  $9.8^{\circ}$ . Incidentally, the value quoted by Freudenberg for the same solvent ( $+ 14.3^{\circ}$ ) is intermediate between these extremes and corresponds to the readings obtained 40 minutes after the solution was prepared. The change, as shown by the diagram reproduced below, was complete in 100 minutes and this comparatively rapid mutarotation in an anhydrous solvent suggests that in addition to the interchange of the hydrogen and hydroxyl of the reducing position other factors may be operative.

On the whole, the results quoted above are regular, but the use of absolute alcohol as the solvent gave a negative result, the initial value ( $[\alpha]_D + 15.9^{\circ}$ ) remaining constant and showing very little change on the addition of a trace of alkali. Reasons exist for the opinion that in this solvent the mutarotation is so rapid as to be undetectable and, in the circumstances, little success was anticipated in the case of aqueous solutions, particularly as only low concentrations are then possible. The result was, however, positive and the specific rotation diminished from  $+ 11.9^{\circ}$ , became *laevo*, and finally attained equilibrium when a small dextrorotation was just detectable. This consecutive fall and rise in activity shows that the mutarotation involves at least two reactions. If water plays a

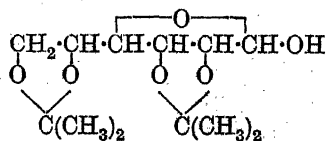
\* Judging from published accounts, it would appear that experiments on mutarotation are frequently vitiated by the excessive use of alkali. In the sugar group particularly, this practice is regrettable, as prolonged changes in activity may thus be promoted which have no relationship to mutarotation in the accepted sense of the expression.

specific as well as a catalytic part in the changes, any compound thus produced must be unstable, as the original mannose diacetone was isolated from the solution by extraction with chloroform after mutarotation was complete. Additional information bearing on this point was obtained from the examination of a solution in 50% alcohol which had attained the permanent specific rotation of  $+8.5^\circ$ . On increasing the aqueous concentration to 75%, the activity was much reduced and ultimately vanished.

FIG. 2.

*Mutarotation of mannose diacetone.*

The combined results, when plotted on curves, suggest that the constitution of mannose diacetone is more complex than is generally supposed. As already stated, our opinion is that the compound is derived from  $\gamma$ -mannose, and this is supported by other results, obtained in this laboratory but still unpublished, which prove definitely that glucose diacetone is a derivative of  $\gamma$ -glucose. There remains, however, the problem as to why  $\gamma$ -glucose condenses with acetone to give a compound in which the reducing group is substituted while the same group, usually the most reactive in the molecule, remains free in the case of  $\gamma$ -mannose. For the time being, the formula for mannose diacetone which finds most favour represents the compound as :



Considering recent views as to the structure of the stable and unstable varieties of mannose, it is possible that the above constitution is approximately correct, and it is our intention to investigate the subject further. Meanwhile it may be said that Ohle's criticism of Haworth's conclusions as to the ring structure of mannose is not justified, as evidently the acetone derivatives of the sugar have no relationship with the amyleno-oxidic variety of the hexose.

### EXPERIMENTAL.

The mannose diacetone was prepared by the standard method and purified by recrystallisation from light petroleum (b. p. 40–70°) diluted with 20% of dry ether. After the second crystallisation the m. p. was 122°, and this remained unaltered on further crystallisation or on subliming the compound in a vacuum. A Zeisel estimation, carried out as a check on the purity of the reagents used in the preparation, gave a negative result and the absence of any action upon Fehling's solution was also confirmed.

#### *Rotation and Mutarotation of Mannose Diacetone.*

*Solvent, acetone.* As the compound displays suspended mutarotation in acetone, this solvent was employed in determining the standard specific rotation.

I. The mannose diacetone was recrystallised three times and thereafter sublimed by heating for 5 hours at 120°/0.2 mm.  $c = 1.016$ ;  $[\alpha]_D^{14} = +38.4^\circ$ . This value remained unchanged for 80 minutes.

II. In this experiment the sublimation process was omitted.  $c = 1.559$ .

Time from start.	$[\alpha]_D^{14}$ .	Time from start.	$[\alpha]_D^{14}$ .
8 minutes	+ 27.9°	4½ hours	+ 27.1°
25     "	27.9	8     "	27.2
75     "	27.5	24    "	26.9
150    "	27.1	30    "	26.8

On adding a trace of sodium hydroxide the specific rotation diminished steadily to the constant value + 16.9°, which was reached in 6 hours. The material recovered from this experiment melted at 123°.

*Solvent, acetylene tetrachloride.* This solvent was selected as it was employed by Freudenberg when he obtained the value  $[\alpha]_{H_2O, \text{yellow}} = +14.3^\circ$ . We find that when the mannose diacetone was recrystallised three times and dried at 80°/15 mm. before use, the maximum initial specific rotation observed was  $[\alpha]_{H_2O}^{15} =$

+26.2° and regular mutarotation ensued. Typical figures are given.  $c = 1.980$ .

Time from start.	$[\alpha]_D^{15^\circ}$ .	Time from start.	$[\alpha]_D^{15^\circ}$ .
5 minutes	+22.6°	60 minutes	+11.6°
15 "	18.6	75 "	10.0
20 "	17.1	90 "	9.6
40 "	14.1	100 "	9.1
50 "	12.6	24 hours	9.1

The above values were verified on four occasions and the figure quoted by Freudenberg corresponds with observations made 40 minutes after the first contact of solvent and solute.

A more striking result was obtained with mannose diacetone which had been sublimed by heating for 5 hours at 120°/0.2 mm.  $c = 0.509$ .

Time from start (mins.) . . . . .	10	15	25
$[\alpha]_D^{14^\circ}$ .....	+31.5°	+27.5°	+21.6°
Time from start (mins.) . . . . .	35	45	55
$[\alpha]_D^{14^\circ}$ .....	+15.7°	+11.8°	+9.8° (constant)

*Solvent, absolute alcohol.* Recrystallised material was used.  $c = 2.574$ . The initial specific rotation was +15.9° and this remained unaffected for 150 minutes. After adding a trace of sodium hydroxide the optical value diminished very slowly.

Time (mins.) .....	5	30	150	300	48 (hours)
$[\alpha]_D^{15^\circ}$ .....	+15.8°	+15.7°	+14.5°	+14.0°	+13.6° (constant)

The dissolved material was recovered and, after recrystallisation, proved to be unaltered mannose diacetone.

*Solvent, water.* Recrystallised material was used and, owing to the limited solubility, only dilute solutions were available. Mutarotation was exceedingly rapid and consequently the initial values varied considerably, but the most striking feature of the optical changes was the inversion of sign and the subsequent return to a small dextrorotation. This is illustrated in the following typical case.  $c = 0.4455$ .

Time from start.	$[\alpha]_D^{16^\circ}$ .	Time from start.	$[\alpha]_D^{16^\circ}$ .
5 minutes	+11.9°	1 hour	-5.6°
15 "	5.6	2 hours	-0.6
25 "	3.6	3½ "	Inactive
35 "	2.8	45 "	+1.1°

The end value remained constant for 8 hours after the addition of a trace of alkali.

Although the development of a levorotation was not observed on every occasion, the initial dextro-value always diminished and thereafter increased. By extraction with chloroform, the dis-

solved material was recovered and, after recrystallisation, was proved to be unchanged mannose diacetone.

*Solvent, 50% aqueous alcohol.* Freudenberg has already recorded that mannose diacetone preserves a constant specific rotation in this solvent for the first 24 hours and that thereafter the value falls to  $+9.2^\circ$ . For  $c = 1.2525$  and  $T = 13^\circ$  we found that in 3 days the end-point was  $[\alpha]_D + 8.5^\circ$  and that very little further alteration took place when a trace of dilute alkali was added. On halving the concentration by the addition of water, the liquid showed  $[\alpha]_D + 0.5^\circ$  and became inactive in the course of 2 hours.

*Condensation of Mannose Diacetone with Phenylhydrazine.*—A 3.5% solution of mannose diacetone was prepared in absolute alcohol containing recrystallised redistilled phenylhydrazine (1 mol. plus 10% excess). The solution was preserved at  $12^\circ$  in the dark, polarimetric readings being taken at intervals.

Time from start.	$[\alpha]_D^{12^\circ}$ .	Time from start.	$[\alpha]_D^{12^\circ}$ .
0 minute	$+18.0^\circ$	10 days	$+8.4^\circ$
2 days	13.3	14 "	9.8
4 "	8.7	19 "	12.7
6 "	4.2	28 "	15.5
7 "	7.0		

The results are typical of the condensation of a reducing sugar with the base, and indicate the superposition of an initial rapid reaction on a subsequent slower change. On isolation in the usual manner, the phenylhydrazone proved to be a syrup, which was not further examined.

*Condensation of Mannose Diacetone with Aniline.*—A 3.6% solution of mannose diacetone in absolute alcohol containing five times the theoretical amount of pure aniline was preserved in the dark at the temperature of the room. Polarimetric readings showed that two consecutive reactions then ensued.

Time from start.	$[\alpha]_D$ .	Time from start.	$[\alpha]_D$ .
0 minute	$+16.5^\circ$	10 days	$+50.5^\circ$
1 day	16.6	12 "	56.4
3 days	27.6	14 "	58.6
6 "	37.9	17 "	63.1

At this stage the crystalline product began to separate and the liquid after filtration was concentrated to a small bulk at  $15^\circ/15$  mm. Clusters of needles were thus obtained in excellent yield and, after purification from light petroleum, the product melted at  $114^\circ$  (Found: C, 64.7; H, 7.6; N, 4.2. Calc. for mannose diacetone anilide, C, 64.5; H, 7.5; N, 4.2%). Mannose diacetone anilide is laevorotatory, but, in common with sugar anilides generally, displayed extensive mutarotation in absolute alcohol.



Time from start.	$[\alpha]_D^{17}$ .	Time from start.	$[\alpha]_D$ .
5 minutes	-118.3°	50 hours	Inactive
15 "	118.3	4 days	+39.8°
50 "	106.9	5 "	50.2
180 "	88.7	6 "	72.8
5 hours	69.4	8 "	79.6
20 "	22.7	12 "	83.0
30 "	12.5		(constant)

The results when plotted on a curve showed a marked resemblance to those given by mannose anilide, although the whole of the rotations are shifted markedly in the dextro-direction. The anilide was recovered unchanged from the above solution.

*Condensation of Methyl Alcohol with Mannose Diacetone.*—A 3% solution of mannose diacetone in dry methyl alcohol containing 0.1% of hydrogen chloride was maintained at 17°, polarimetric readings being taken at intervals.

Time from start.	$[\alpha]_D^{17}$ .	Time from start.	$[\alpha]_D^{17}$ .
0 minute	+13.6°	8 hours	+18.9°
2 hours	16.0	24 "	21.1
3 "	17.1	48 "	21.7
4 "	17.9	72 "	21.7

The acid was removed with silver carbonate, and the filtrate taken to dryness in a high vacuum, the residue then remaining being extracted repeatedly with dry ethyl acetate in the cold. On removal of the solvent under diminished pressure a syrup was obtained which, as it reduced Fehling's solution slightly, was taken up in cold ether and filtered from a small quantity of reducing material. The ether was then evaporated and the syrup isolated by redistillation, a fraction, b. p. 115—125°/0.3—0.7 mm., being collected. The distillate consisted of a mixture of methylmannoside diacetone (64%) and unchanged mannose diacetone (36%). The conditions of the condensation with acid methyl alcohol were varied, and it was ascertained that when the reaction was continued until all the mannose diacetone had disappeared, the bulk of the product then consisted of  $\gamma$ -methylmannoside. This was isolated by solution in cold ethyl acetate, the syrup thus extracted being afterwards treated with ether to remove extraneous products. The mannoside was obtained as a colourless syrup which slowly crystallised owing to its spontaneous conversion into the  $\alpha$ -form.

Acknowledgment is made to the Department of Scientific and Industrial Research for a grant awarded to one of us.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,

UNIVERSITY OF ST. ANDREWS.

[Received, March 2nd, 1926.]

CXLII.—*Ethyl Hydrogen Sulphate. Part II.*

By M. ABDUL HAMID, KIRPAL SINGH, and HORACE BARRATT DUNNICLIFF.

SEVERAL subjects not investigated by Dunnicliff and Butler (J., 1921, 119, 1384) have been studied.

*Preparation of Ethyl Hydrogen Sulphate.*—Attempts to prepare the pure ester have been made by the following methods :

1. By the action of hydrogen sulphide on lead ethyl sulphate (a) dry, (b) in alcoholic solution, and (c) suspended in ether. No action took place in the absence of water.

2. Passing ethylene into (a) sulphuric acid, (b) an ethereal solution of sulphuric acid, and (c) alcoholic sulphuric acid. Only very impure products were obtained.

3. Extraction of such sulphates as  $\text{Ag}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ ,  $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$ , and  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$  gave a mixture of sulphuric acid and ethyl hydrogen sulphate in ether.

4. Barium ethyl sulphate,  $\text{Ba}(\text{C}_2\text{H}_5\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , was prepared in the ordinary way. On treatment with dry alcohol, the anhydrous salt,  $\text{Ba}(\text{C}_2\text{H}_5\text{SO}_4)_2$ , was formed. In order to start with an alcoholic sulphuric acid in which the free sulphuric acid was a minimum, 20% alcoholic sulphuric acid was taken after standing for a month. The percentage esterification of the sulphuric acid was 85. The free sulphuric acid was estimated. Barium ethyl sulphate in excess of the calculated amount required to react with the free sulphuric acid present was added to a weighed quantity of the alcoholic sulphuric acid and well shaken. The mixture was filtered and the filtrate heated with excess of barium ethyl sulphate under reduced pressure on a water-bath. When no more distillate was obtained, the residue in the flask was (a) filtered off or (b) extracted with dry ether in an apparatus of the Soxhlet type specially arranged for the extraction of liquids. It was hoped that the filtrate from (a) and the residue after driving off the ether from (b) would be free from sulphuric acid and probably from water and alcohol.

Among a large number of determinations of the equivalent weight of the ester so prepared, nine samples gave values which were within experimental error of the theoretical value, 126. The others were either high or low. The ester darkened on standing and the equivalent weight fell owing to the formation of free sulphuric acid. After some months, some preparations became black and free carbon was among the products of decomposition.

Attempts were made to determine the composition of several of the samples by combining the results of analyses by combustion,

estimation of sulphate by the barium sulphate method, and determination of esterification by the volumetric method. The greatest degree of purity obtained showed a yield of 84.5% of ester. A typical analysis was: Equivalent weight, 126.  $C_2H_5 \cdot HSO_4$ , 64.9;  $H_2SO_4$ , 13.7;  $C_2H_5 \cdot OH$ , 10.0;  $H_2O$ , 11.8; total, 100.4%.

5. By the action of dry hydrogen chloride on anhydrous barium ethyl sulphate (a) dry, (b) in anhydrous alcoholic solution, and (c) in ethereal solution. In the dry state no appreciable action was observed. In alcoholic and ethereal solution the hydrogen chloride reacted with the salt, giving insoluble barium chloride and ethyl hydrogen sulphate in solution. At first sulphuric acid was absent but, on concentration either by evaporation or water-bath or at the ordinary temperature in a desiccator, the ester decomposed. The solution, at first colourless, slowly turned yellow with increasing concentration and, long before the solvent was driven off, a strong test for sulphuric acid was obtained. This decomposition was not due to the presence of hydrochloric acid, because the same result was obtained in the presence of excess of barium ethyl sulphate. The potassium salt behaves in a similar manner.

All attempts to prepare pure ethyl hydrogen sulphate have failed. The ester appears to become more unstable with increasing concentration.

*Solubility of Ethyl Hydrogen Sulphate in Ether.*—Most books of reference state that ethyl hydrogen sulphate is insoluble in ether. Since pure ethyl hydrogen sulphate has not been prepared, it is difficult to say if this is so, as all ethereal solutions of the ester in ether contain some sulphuric acid. Determinations of the solubility of the ester at 30° in presence of a small percentage of sulphuric acid show that the concentration of the ethyl hydrogen sulphate diminishes as the concentration of free sulphuric acid rises. Extrapolation of the results indicates that the solubility of pure ethyl hydrogen sulphate in pure ether should be about 1.27 g. of ester per 100 g. of dry ether at 30°.

TABLE I.

*Solubility of Ethyl Hydrogen Sulphate in Ether containing free Sulphuric Acid at 30°.*

Free $H_2SO_4$ %	0.092	0.152	0.186	0.314	0.372	0.516	0.533
$C_2H_5 \cdot HSO_4$ %	1.125	1.061	0.999	0.818	0.722	0.509	0.470

These points lie practically on a straight line, but as the concentration of the sulphuric acid increases, the relationship is not so simple, e.g., when the concentration of sulphuric acid is 4.06%.

the concentration of the ester is 0.242%. If the solution were kept for some time, the concentration of the ester would increase on account of the interaction between ether and sulphuric acid. At the very low concentrations given in the table, the rate of esterification would be very slow and the total esterification very small. As the solutions were estimated immediately after they were formed, the line obtained by plotting the above points may be correctly described as a solubility graph. The fact that ethyl hydrogen sulphate is soluble in ether may be demonstrated by extracting ethyl hydrogen sulphate in a Soxhlet apparatus. The liquid in syphons over eventually separates into two layers, a lower one in ethyl hydrogen sulphate and an upper one poor in the ester. If the upper one be separated and allowed to evaporate, the ether first becomes cloudy and then a heavy layer of impure ethyl hydrogen sulphate separates.

*The Order of the Reaction between Ethyl Alcohol and Sulphuric Acid at High Concentrations of Acid.*—In the previous work, the velocity of the reaction at concentrations of sulphuric acid above 13.18% was not studied. The order of the reaction at concentrations of sulphuric acid between 60 and 75% has now been investigated. The practical difficulties encountered in this work were very considerable. At 18°, the reaction is very violent, so the experiments were carried out at 0°. In order to mix the interacting substances, alcohol which had been cooled to -5° was added slowly to super-cooled sulphuric acid. At the highest concentration, the acid was cooled to -10° and great care had to be exercised to prevent it from crystallising out. After the alcohol had been added there was no fear of this. The ingredients were thoroughly mixed, the flask being always immersed in the freezing mixture. When all the alcohol had been added, the reaction vessel was transferred to a bowl containing clean crushed ice. As soon as the temperature of the reaction mixture rose to 0°, the first portion of the reaction mixture was withdrawn in an ice-cold 1 c.c. pipette and run into a known quantity of standard caustic soda more than sufficient to neutralise it, and its weight was determined. The proportions in which the sulphuric acid and alcohol had been mixed in the reaction mixture were estimated after the experiment. The esterification was measured and the value of  $z$ , the time to be added to the observed time to compensate for the disturbed period, was calculated as previously described (*loc. cit.*, p. 1390).

The object was to obtain :

1. A minimal esterification during the disturbed period.
2. As large a difference as possible between the actual time of observation,  $t$ , and the correction,  $z$ , to be added.

3. A final total esterification several multiples of the esterification during the disturbed period.

The results in Tables II to IV show conclusively that, as in the case of low concentrations of sulphuric acid, the reaction is of the first order even when 1.44 molecules of sulphuric acid are mixed with one of alcohol, forming an alcoholic sulphuric acid containing 74.45% of sulphuric acid.

$x$  = quantity of ethyl hydrogen sulphate expressed as g.-mol. per 100 g. of mixture, and  $t$  = the actual time.

$$k = \{1/(t + z)\} \log \{a/(a - x)\}.$$

TABLE II.

Sulphuric acid = 60.00% = 0.612 g.-mol. = $a$ .							
Ethyl alcohol = 40.00% = 0.869 g.-mol. $z$ = 2.4 hrs.							
$x$ .	$t$ (hrs.).	$t + z$ .	$k \times 10^3$ .	$x$ .	$t$ (hrs.).	$t + z$ .	$k \times 10^3$ .
0.054	—	2.40	16.7	0.112	2.90	5.30	17.2
0.087	1.35	3.75	17.2	0.122	3.78	6.18	15.6
0.099	2.20	4.60	16.7	0.134	4.45	6.85	15.7
							Mean 16.5

TABLE III.

Sulphuric acid = 68.14% = 0.695 g.-mol. = $a$ .							
Ethyl alcohol = 31.86% = 0.693 g.-mol. $z$ = 87.6 mins.							
$x$ .	$t$ (mins.).	$t + z$ .	$k \times 10^3$ .	$x$ .	$t$ (mins.).	$t + z$ .	$k \times 10^3$ .
0.136	—	87.6	1.08	0.292	137.5	225.1	1.05
0.201	45.8	133.4	1.11	0.330	193.2	280.8	1.00
0.267	105.5	193.1	1.09	0.349	210.0	297.6	1.02
							Mean 1.06

TABLE IV.

Sulphuric acid = 75.45% = 0.770 g.-mol. = $a$ .							
Ethyl alcohol = 24.55% = 0.534 g.-mol. $z$ = 85 mins.							
$x$ .	$t$ (mins.).	$t + z$ .	$k \times 10^3$ .	$x$ .	$t$ (mins.).	$t + z$ .	$k \times 10^3$ .
0.187	—	85.0	1.42	0.313	77.5	162.5	1.45
0.245	31.0	116.0	1.43	0.332	103.5	188.5	1.30
0.284	52.0	137.0	1.46				Mean 1.41

The mass-action coefficient obtained after 1 molecule of sulphuric acid had been allowed to interact with 1.05 molecules of alcohol at laboratory temperature for 25 days was 0.5650, and the ethyl hydrogen sulphate formed corresponded with 0.5787 g.-mol. These values are in agreement with (a) the "calculated" esterification (*loc. cit.*, p. 1387), which was 0.5595 g.-mol., (b) the variation in the value of the mass-action coefficient as explained in equation (3) (*loc. cit.*) and the general proposition that the ratio

$$\frac{\text{actual esterification obtained}}{\text{maximum possible esterification}} = 0.5787 \text{ (observed)}$$

is a minimum when equimolecular proportions of the reacting

compounds are employed. Claesson (*J. pr. Chem.*, 1879, **19**, 246) obtained the value 0.5710.

In some preliminary experiments it appeared that the final maximum esterification in an alcoholic sulphuric acid made by treating sodium hydrogen sulphate with dry alcohol was less than that found in an alcoholic sulphuric acid of the same strength made by mixing the constituents directly and that this was due to the presence of some sulphate of sodium in the first case. This has now been shown to be erroneous as instanced by the examples given below:

$\text{H}_2\text{SO}_4$ % in the alcoholic sulphuric acid containing sodium sulphate.	$\text{C}_2\text{H}_5\cdot\text{HSO}_4$ % found.	Theoretical % of $\text{C}_2\text{H}_5\cdot\text{HSO}_4$ for alcoholic $\text{H}_2\text{SO}_4$ .
9.46	10.16	10.08
12.86	13.87	14.06
43.50	44.16	44.36

### Summary.

All attempts to prepare pure ethyl hydrogen sulphate have been unsuccessful.

From determinations at  $0^\circ$  of the velocity coefficients of the reaction between sulphuric acid and alcohol in which the concentration of sulphuric acid is from 60 to 75%, it is shown that the reaction is of the first order.

The solubility of ethyl hydrogen sulphate in ether containing small quantities of sulphuric acid has been determined at  $30^\circ$ .

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## CXLIII.—*The Reactivity of Alkyl Iodides with Sodium Benzyl Oxide. A Criticism.*

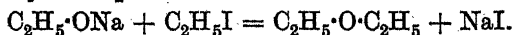
By LEONARD JAMES GOLDSWORTHY.

THE reactivity of alkyl iodides with sodium benzyl oxide and the effect of temperature on such reactions were studied by Haywood (*J.*, 1922, **121**, 1904), whose reaction mixture consisted of equal volumes of  $N/5$ -alcoholic solutions of sodium benzyl oxide and alkyl iodide. As the molecular ratio of ethyl alcohol to sodium benzyl oxide in such a mixture is about 170, it is extremely improbable that Haywood's velocity coefficients can be a measure of the rate of the reaction  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{ONa} + \text{RI} = \text{NaI} + \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OR}$ . It is more likely that in such a mixture the concentration of sodium ethoxide is much greater than the concentration of sodium benzyl oxide, and that the velocity measured by Haywood was really that

of the reaction  $C_2H_5 \cdot ONa + RI = NaI + C_2H_5 \cdot OR$ . Although he remarked that alcoholysis "to a certain extent" is to be expected, Haywood apparently did not realise the probability that under the conditions of his experiments alcoholysis would be almost complete.

In order to put the matter to the test, the author mixed equal volumes of *N*/5-ethyl-alcoholic solutions of sodium ethoxide and ethyl iodide and compared the rate of the reaction in this mixture at 35° with the rate of the reaction in a mixture of equal volumes of *N*/5-ethyl-alcoholic solutions of sodium benzyl oxide and ethyl iodide. The velocity coefficients in the two experiments were practically identical. As there was a possibility that this result might have been due to coincidence, the reactivities of sodium benzyl oxide and sodium ethoxide being the same in ethyl-alcoholic solution, two further experiments were performed, in which *n*-butyl alcohol was used as solvent in the place of ethyl alcohol. Here again the velocity of the reaction in a mixture of equal volumes of *N*/5-butyl-alcoholic solutions of sodium butyl oxide and ethyl iodide was practically the same as the velocity in a mixture of equal volumes of *N*/5-butyl-alcoholic solutions of sodium benzyl oxide and ethyl iodide.

A final experiment was performed as a crucial test, the object of which was to isolate and examine the products of the reaction. A solution prepared by mixing equal volumes of 2*N*-ethyl-alcoholic solutions of sodium benzyl oxide and ethyl iodide was fractionally distilled after sufficient time had elapsed for the completion of the reaction (at 35°). If in this experiment no ethyl benzyl ether had been formed, the sole reaction being that between sodium ethoxide and ethyl iodide, 14.8 g. of ethyl ether should have been formed. Actually 11 g. of liquid boiling below 45° were collected and from this 6 g. of pure ethyl ether were obtained by further fractionation. Thus it is clear that even in a normal ethyl-alcoholic solution of sodium benzyl oxide and ethyl iodide the main reaction is that represented by the equation



In Haywood's experiments, in which the concentrations were tenth-normal, the amount of ethyl benzyl ether formed must have been negligibly small.

#### EXPERIMENTAL.

The ethyl alcohol used in these experiments was commercial absolute alcohol, dried by digesting with lime and calcium. The ethyl iodide (Kahlbaum's) was purified just before use by washing with dilute alkali and water, drying over calcium chloride, and distilling from silver powder.

The benzyl alcohol (Kahlbaum's) was redistilled before use. The *n*-butyl alcohol was purified by distillation, after treatment with lime.

All the instruments used were standardised with reference to standard instruments.

During the velocity determinations the temperature, kept constant by means of a thermostat provided with an Ostwald toluene regulator and stirrer, did not vary more than 0.05°. In the preparation of the *N*/5-ethyl-alcoholic solution of sodium benzyl oxide, a weighed quantity of benzyl alcohol was mixed with a measured volume of a standard alcoholic solution of sodium ethoxide, containing an equivalent quantity of the ethoxide. The mixture was then diluted to the calculated volume with alcohol. The solution of sodium benzyl oxide in butyl alcohol was similarly prepared. The rates of reaction were measured in the manner described by Haywood.

**Results.**—The velocity coefficients are calculated from the formula  $k = \frac{1}{t} \cdot \frac{x}{a-x} \cdot \frac{y}{C_0 a}$ , in which *x*, *y*, *t*, *a* and *C*<sub>0</sub> have the same significance as in Haywood's paper.

*N*/40-Hydrochloric acid was used in the titrations.

**1st Expt.** Equal volumes of *N*/5-sodium benzyl oxide (in ethyl alcohol) and *N*/5-ethyl iodide (in ethyl alcohol).

Temp. 35°. Zero = 35.40 c.c.  
*y* = 38.45 c.c.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>x</i> .	<i>k</i> × 10 <sup>4</sup> .
120	27.33	8.07	267
234	23.06	12.34	248
326	20.02	15.38	256
441	17.50	17.90	252
Mean			256

**2nd Expt.** Equal volumes of *N*/5-sodium ethoxide (in ethyl alcohol) and *N*/5-ethyl iodide (in ethyl alcohol).

Temp. 35°. Zero = 35.40 c.c.  
*y* = 40.00 c.c.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>x</i> .	<i>k</i> × 10 <sup>4</sup> .
45	32.00	3.40	267
101	28.75	6.65	259
248	22.50	12.90	261
319	20.45	14.95	259
Mean			262

**3rd Expt.** Equal volumes of *N*/5-sodium benzyl oxide (in *n*-butyl alcohol) and *N*/5-ethyl iodide (in *n*-butyl alcohol).

Temp. 35°. Zero = 36.82 c.c.  
*y* = 39.84 c.c.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>x</i> .	<i>k</i> × 10 <sup>4</sup> .
62	33.40	3.42	178 *
187	28.80	8.02	160
352	24.60	12.22	152
Mean			156

**4th Expt.** Equal volumes of *N*/5-sodium *n*-butoxide (in *n*-butyl alcohol) and *N*/5-ethyl iodide (in *n*-butyl alcohol).

Temp. 35°. Zero = 36.9 c.c.  
*y* = 40.00 c.c.

<i>t</i> .	<i>a</i> - <i>x</i> .	<i>x</i> .	<i>k</i> × 10 <sup>4</sup> .
90	32.32	4.58	169
150	29.95	6.95	166
273	26.35	10.55	158
419	23.10	13.80	153
Mean			159

\* Omitted in calculating the mean.



CXLIV.—*The Rate of Reaction between Formic Acid and Iodine in Aqueous Solution.*

By DALZIEL LLEWELLYN HAMMICK and MICHAEL ZVEGINTZOV.

It has been shown (Hammick, Hutchison, and Snell, J., 1925, 127, 2715) that the rate of reaction between bromine and formic acid is represented by the mass-action equation

$$dx/dt = k[\text{H}\cdot\text{COO}'][\text{X}]/\{1 + [\text{X}']/K_1\} \dots \dots (1)$$

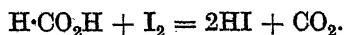
in which  $[\text{X}]$  is the total concentration of free halogen  $\text{X}_2 + \text{X}'_3$ ,  $[\text{X}']$  the concentration of halogen ion, and  $K_1$  is the equilibrium constant  $K_1 = [\text{X}_2][\text{X}']/[\text{X}'_3]$ . For bromine,  $1/K_1$  is of the order of 10 and  $[\text{Br}']/K_1$  could not be neglected in comparison with unity. In chlorine and iodine, however, we have two extreme cases. For chlorine,  $K_1$  is large and  $[\text{Cl}']/K_1$  can be neglected; for iodine,  $K_1$  is small and has the value  $1.75 \times 10^{-3}$  at  $45^\circ$  (Fedotiev, *Z. physikal. Chem.*, 1909, 69, 22) and  $1.365 \times 10^{-3}$  at  $25^\circ$  (Jakowkin, *ibid.*, 1896, 20, 19). Hence in the case of iodine we may neglect unity in comparison with  $[\text{I}']/K_1$  and we should expect to find that, whereas the rate of reaction between chlorine and formic acid would be practically independent of chlorine-ion concentration, that between iodine and formic acid would be inversely proportional to the concentration of iodine ion. That is to say,

$$dx/dt = k[\text{H}\cdot\text{COO}'][\text{I}]/\{[\text{I}']/K_1\} \dots \dots (1A)$$

should represent the course of the reaction in the latter case. Iodine reacts at  $60^\circ$  at a convenient rate and results have been obtained at that temperature that confirm the conclusion arrived at above.

Iodine and formic acid, in the presence of potassium iodide, were mixed in a glass stoppered flask in a thermostat maintained at  $61.5^\circ \pm 0.25^\circ$ , the iodine being estimated from time to time with standard thiosulphate. In all experiments, the potassium iodide was present in excess (never less than 10 to 1) sufficient to eliminate perturbations due to the iodine ion produced during the reaction. A zero time-correction was obtained by plotting  $\log a/(a - x)$  against time and extrapolating to zero time. The unimolecular velocity coefficients given below have been corrected in this way.

By analogy with the reaction between bromine and formic acid, it is to be expected that iodine would react as follows:



An experiment was therefore carried out by mixing equal volumes of equivalent solutions of formic acid and iodine in presence of

excess of potassium iodide and measuring the rate of disappearance of the iodine. The results show that the reaction is bimolecular, as the above equation suggests.

TABLE I.

$[\text{H}\cdot\text{CO}_2\text{H}] = N/100$ .  $[\text{I}_2] = N/100$ .  $a - x$  = thiosulphate titre at time  $t$ .

$t$ (mins).	$a - x$ .	$1/(a - x) - 1/a$ .	$k \times 10^3$ (bimol. coeff.).
0.0	10.9	—	—
4.53	10.65	0.00215	4.45
10.08	10.4	0.00441	4.37
19.42	9.95	0.00826	4.51
25.6	9.7	0.01146	4.48

*Influence of Formic Acid Concentration on the Rate of Disappearance of Iodine.*—In Table II are the results of a series of determinations of the unimolecular velocity coefficient for two different concentrations of formic acid.

TABLE II.

$[\text{H}\cdot\text{CO}_2\text{H}]$ .	$[\text{KI}]$ .	$[\text{I}_2]$ .	$k \times 10^3$ .	
$N/3$	0.117N	0.011N	9.15	ratio = 1.34
$2N/3$	0.117	0.011	12.2	
$N/3$	0.234	0.011	4.65	" 1.37
$2N/3$	0.234	0.011	6.35	
$N/3$	0.17	0.016	5.85	" 1.45
$2N/3$	0.17	0.016	8.47	

Since formic acid obeys the dilution law, we have approximately  $\alpha^2/V = K_a$ , where  $\alpha$  is the degree of dissociation,  $V$  is the dilution, and  $K_a$  is the dissociation constant; hence, for any two dilutions  $V_1$  and  $V_2$ , we have  $\alpha_1/\alpha_2 = \sqrt{V_1/V_2}$ . Thus  $[\text{H}\cdot\text{COO}' ]_1/[\text{H}\cdot\text{COO}' ]_2 = (\alpha_1/V_1)/(\alpha_2/V_2) = \sqrt{V_2/V_1}$ . For the pairs of velocity coefficients given in Table II,  $V_2/V_1 = 1/2$  and hence  $[\text{H}\cdot\text{COO}' ]_2/[\text{H}\cdot\text{COO}' ]_1 = \sqrt{2} = 1.41$ . If the rate of reaction is proportional to  $[\text{H}\cdot\text{COO}' ]$  we should expect to find that doubling the concentration of formic acid would increase the velocity coefficient in the ratio of 1 to 1.41. The mean of the ratios in Table II is 1.39.

*Influence of Hydrogen-ion Concentration.*—Unimolecular velocity coefficients were determined in the presence of varying quantities of hydrochloric acid. The results of a series of determinations are summarised in Table III.

TABLE III.

$[\text{HCl}]$ .	$a$ .	$[\text{H}]$ .	$k \times 10^3$ .	$k \times [\text{H}] \times 10^3$ .
0.066N	0.844	0.06N	3.5	0.210
0.132	0.812	0.11	1.9	0.209
0.198	0.786	0.16	1.19	0.191

Under  $a$  are the activity coefficients of hydrochloric acid (Ellis, *J. Amer. Chem. Soc.*, 1916, 38, 535; Noyes, *ibid.*, 1917, 39, 2532).

These figures refer to acid at room temperature; in using them at 60°, we are, of course, assuming that the ratios of activity coefficients corresponding to different concentrations are independent of temperature. Under  $[H]$  are effective concentrations of hydrogen ion, calculated from the Law of Mixed Acids (Lewis, "System of Physical Chemistry," 1921, Vol. 1, p. 255) by the formula  $[H] = K_a/\alpha[HCl]$ ; the dissociation constant for formic acid,  $K_a$ , is taken as  $2.1 \times 10^{-4}$  (Ostwald, *Z. physikal. Chem.*, 1889, 3, 239); this value refers to 18° and hence values of  $[H]$  can only be regarded as relative. Nevertheless, the constancy of the product  $k \times [H]$  shows that the velocity of the reaction is inversely proportional to the effective concentration of the hydrogen ion and therefore directly proportional to the concentration of formyl ion.

*Influence of Iodine-ion Concentration.*—The concentration of iodine ion was varied between 0.117*N* and 0.350*N* by the addition of potassium iodide and was always in excess sufficient to mask the effect of the iodine ion produced in the course of the reaction. The results are in Table IV.

TABLE IV.  
 $[H \cdot CO_2H] = N/3$ .

$[I_2]$ .	$[KI]$ .	$k \times 10^2$ .	$\alpha$ .	$k \times \alpha \times [KI] \times 10^3$ .
0.012 <i>N</i>	0.117 <i>N</i>	0.915	0.735	0.786
0.11	0.234	0.465	0.689	0.750
0.11	0.351	0.328	0.663	0.762
0.16	0.170	0.585	0.710	0.733
0.0275	0.292	0.372	0.655	0.733
0.0335	0.351	0.330	0.663	0.768

The values for the activity coefficient,  $\alpha$ , are from McInnes and Parker (*J. Amer. Chem. Soc.*, 1915, 37, 1445) for potassium chloride in the presence of hydrogen ion, no data being available for the activity of the iodine ion. The close similarity of the potassium chloride and potassium bromide values renders the use of potassium chloride values justifiable. The figures do not refer to 60°, and hence are assumed to be only relatively correct. The product in column 5 shows that the rate of reaction is inversely proportional to the effective concentration of the iodine ion, as predicted by equation (1A).

The reaction between iodine and sodium formate in the presence of potassium iodide has been studied by Dhar (*J.*, 1917, 111, 726). He concludes that interaction takes place between iodine and formyl ions and notices the retarding influence of potassium iodide. He explicitly excludes, however, the possibility that this effect is due to disturbance of the equilibrium  $I_2 + I' \rightleftharpoons I'_3$ , and claims that the potassium iodide acts catalytically. He compares two cases in which "the concentrations of sodiumoformate are equal and according to

the mass-action equilibrium the velocity coefficients should be the same, since the ratio of the concentration of potassium iodide and iodine is the same in the two cases" (*loc. cit.*, p. 730). As a matter of fact, the ratio of the two velocity coefficients is  $k_1/k_2 = 0.00196/0.00378 = 0.52$ . If we now apply equation (1A) to the case of a velocity determination in which  $[\text{H}\cdot\text{COO}']$  and  $[\text{I}']$  are constant (sodium formate and potassium iodide were in excess in Dhar's experiments), we have on integrating,  $(1/t) \log a/(a-x) = k = K \cdot K_1 \cdot [\text{H}\cdot\text{COO}']/[\text{I}']$ . For two experiments in which  $[\text{H}\cdot\text{COO}']$  is the same in each, we have  $k_1/k_2 = [\text{I}']_2/[\text{I}']_1$ . Applying this to Dhar's examples, with the assumption that the potassium iodide is completely dissociated, we find  $k_1/k_2 = 2.7066/5.4132 = 0.50$ , in excellent agreement with the ratio given above. Thus Dhar's results do not, as he concludes, require us to regard the action of the potassium iodide as catalytic, but actually provide very good evidence in support of the view embodied in equations (1) and (1A) above.

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## CXLV.—*The Complexity of the Solid State. Part III.* *The Behaviour of Pure Sulphur Trioxide. Part II.*

By ANDREAS SMITS and PIETER SCHOENMAKER.

CONTINUING our earlier publication on the behaviour of pure sulphur trioxide (J., 1924, 125, 2554) we first conclude the description of our investigation of the ice-like form. Tables VIII and IX of that paper contained the vapour pressures of the solid and the liquid phases of the ice-like form when in inner equilibrium up to  $49.75^\circ$ . We have since determined the vapour pressure of the liquid in inner equilibrium up to  $90^\circ$  with the following results :

$t$ .....	$57.1^\circ$	$65.4^\circ$	$74.0^\circ$	$80.9^\circ$	$90.2^\circ$
$p$ (mm. Hg) .....	1377.2	2041.0	2964.0	3985.5	5794.0

In order to find the point of intersection of the vapour-pressure curves of the solid and the liquid in inner equilibrium we have applied the method already used in the study of phosphorus ("Theory of Allotropy," p. 226; *Z. physikal. Chem.*, 1916, 91, 248). From the equation  $T \ln p = -Q/R + CT$ , it follows that on plotting  $T \ln p$  as a function of  $T$  a straight line will be obtained. The values of  $T \ln p$  for the temperature range  $0-90.2^\circ$  are in the

second column of Table I, and graphical representation gives two straight lines (see Fig. 5, p. 2565, of the earlier paper).

The two straight lines intersect in the triple point  $16.8^\circ$  and  $T \ln p = 1467$ , corresponding with  $p = 158.5$  mm. (Lighty, Berthoud, and Le Blanc found  $16.79^\circ$ ,  $16.85^\circ$ , and  $16.8^\circ$  respectively.) From the slope of the sublimation line, covering the first four temperatures of Table I, it follows that  $C$  for this line is 25.84, and hence the values of  $Q/R$  for the different observation temperatures may be calculated as shown in the third column of Table I. If the mean value of  $Q_{sg}/R$  is taken as 6000, the molecular heat of sublimation,  $Q_{sg}$ , is 11900 cal.

Similarly, the value of  $C$  for the liquid vapour pressure line is found to be 22.7, and the molecular latent heat of evaporation,  $Q_{lg}$ , based on the mean value of  $Q_{lg}/R$  (see Table I), is calculated to be 10100 cal. It further follows that the molecular latent heat of fusion,  $Q_{sl}$ , is 1800 cal. (Le Blanc calculated 2220 cal. from his determinations.)

From our determinations, it appears that the boiling point under a pressure of 760 mm. is  $44.8^\circ$  (compare Buff,  $46-47^\circ$ ; Schultz-Sellock,  $46^\circ$ ; Weber,  $46.2^\circ$ ; Lighty,  $44.88^\circ$ ; Berthoud,  $44.52^\circ$ ), and that the Trouton ratio  $Q_{lg}/T_b = 10100/317.8 = 31.8$ , as compared with the normal value 22. These results indicate that the liquid is more complex than the vapour, and that the solid and liquid phases differ but slightly in complexity. We shall return later to this phenomenon.

TABLE I.

$t$ .	$T \ln p$ .	$Q/R$ .	$t$ .	$T \ln p$ .	$Q/R$ .
0.15°	1043	6015	35.0°	1889	5102.5
5.0	1164	6019	40.5	2010	5106.5
10.2	1299	6019	45.0	2116	5103
15.5	1434	6021	49.75	2222	5104
17.6	1486	5111	57.1	2386	5107
20.5	1553	5109	65.4	2579	5103
22.5	1602	5100	74.0	2774	5103
25.3	1658	5113.5	80.9	2934	5100
30.65	1786	5106	90.2	3147	5100

S + G

L + G

L + G

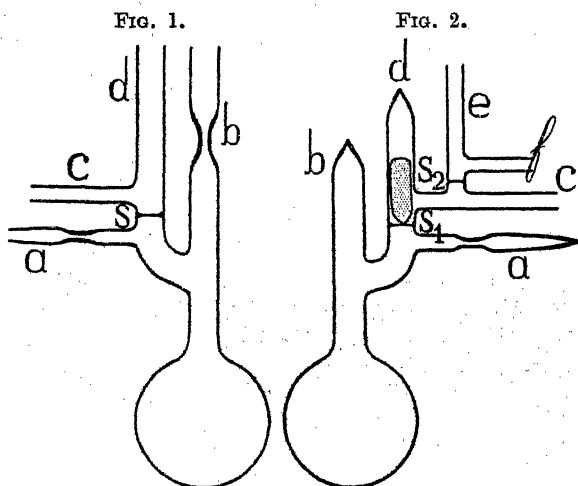
*The Insufficiently Dried, Low-melting, Asbestos-like Form.*

The region of the pseudo-system, in which the ice-form of sulphur trioxide is situated, is that of a dissociable compound of pseudo-components, related to each other as polymerides or isomerides, these terms being used in the widest possible sense (J., 1924, 125, 2554).

The ice-form of sulphur trioxide is one of the two metastable modifications. The other generally constitutes three-quarters of the pure sulphur trioxide in the bulbs supplied by Kahlbaum; it is

like asbestos in appearance and will be referred to as the low-melting, asbestos-like form.

For our more recent work, several bulbs provided with a septum (Fig. 1) were sent to the firm of Kahlbaum and filled with pure sulphur trioxide, the ends of the tubes *a* and *b* then being sealed. Such a bulb, unevacuated, was joined to a high-vacuum pump at *a* by a very short rubber tube connected with a small steel tube about 5 cm. in length, in such a way that *a* was inside the steel tube; by moving this tube the point *a* (previously scratched) could be broken. (To prevent the mercury in the pump from reacting with the sulphur trioxide, a U-tube cooled in liquid air was placed



in front of the pump.) After evacuation, the capillary tube *a* was sealed off.

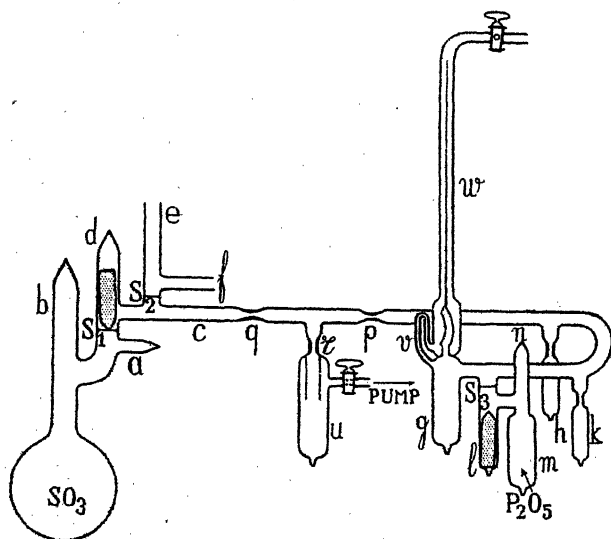
A second T-piece with a septum,  $S_2$ , was now sealed to the delivery tube, a breaker of solid glass carefully placed on the septum  $S_1$  (Fig. 2), and the tube *c* sealed to a glass spring indicator, with the bulb *g* and the mantle *w* still connected through a capillary tube, *v*, as shown in Fig. 3. Bulb *g* was connected to a wide horizontal U-tube to which were sealed two or four vertical tubes, provided with capillaries, and a T-piece with septum,  $S_3$ , with breaker and bulb, *m*. The remaining connexion with the vessel *u* is evident from Fig. 3.

The whole apparatus was heated while a current of dry air was driven through every tube and vessel, and finally the capillary ends of these tubes and vessels were sealed off in succession. The sulphur trioxide bulb being cooled in liquid air, the rest of the apparatus was evacuated by connecting the delivery tube of vessel

*u*, which also was cooled in liquid air, with the high-vacuum pump. When a high vacuum had been reached, communication between the mantle *w* of the glass spring and the vessel *g* was stopped by sealing off the capillary tube *v*. The septum *S*<sub>1</sub> was then broken by shaking the apparatus. By evacuating again, sealing off the capillary *r*, and allowing the sulphur trioxide bulb to attain room temperature, a sufficient portion of the sulphur trioxide was distilled into *g*, this vessel being cooled to  $-80^{\circ}$  in a mixture of solid carbon dioxide and alcohol. The capillaries *p* and *q* were then sealed off.

The further manipulations necessary to make the apparatus ready for vapour-pressure measurements are described in J., 1924, 125, 2554.

FIG. 3.



A part of the sulphur trioxide, obtained in the foregoing way, was the ice-form, for we found the vapour-pressure line of this form to be as if it were in inner equilibrium. This was in complete agreement with the fact that the sulphur trioxide had not been dried by phosphorus pentoxide. After the ice-form had been distilled off by cooling tube *k* in liquid air and sealing, the vapour-tension line was determined again with the following results :

TABLE II.

Temp.	$p$ (mm. Hg).	$T \ln p$ .	$Q/R$ .	Temp.	$p$ (mm. Hg).	$T \ln p$ .	$Q/R$ .
0.2°	33.0	955.3	6574	20.25°	162.8	1494	6588
5.1	49.2	1083	6579	24.85	230.1	1620	6588
10.1	72.3	1212	6590	30.3	334.1	1761	6598
15.0	106.6	1345	6592				

The vapour pressures for the not intensively dried, liquid phase were the values employed in Table I.

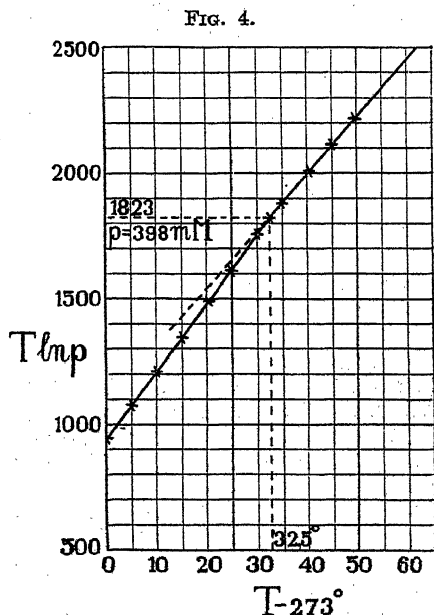
If  $T \ln p$  is plotted against  $T$ , Fig. 4 is obtained, in which two straight lines intersect at  $32.5^\circ$  and  $T \ln p = 1823$  (i.e.,  $p = 398$  mm. Hg). This temperature is the melting point of the low-melting, asbestos-like form under this vapour pressure, if it is in inner equilibrium, or, in other words, if it behaves as a unary substance.

The triple point of the low-melting, asbestos-like form is therefore situated at  $32.5^\circ$  and 398 mm. Hg. The vapour-tension line for

this form indicates that the value of  $C$  in the formula  $T \ln p = -Q/R + CT$  is 27.56. The value of  $Q/R$  at each observation temperature is in Table II, and the mean value may be taken as 6590, whence  $Q_{SG} = 13000$  cal. Since  $Q_{LG} = 10100$  cal. (see p. 1109), it follows that  $Q_{SL} = 2900$  cal.

*The Intensively Dried, Low-melting, Asbestos-like Form.*

The method of intensive drying, as applied with the ice form, is very difficult to carry out in this case, since it is an arduous task to prepare the low-melting, asbestos-like form if the sulphur trioxide has been



intensively dried. We have therefore prepared the not intensively dried, low-melting, asbestos-like form and begun to dry it in the *solid* state, an operation which will take a very long time, perhaps several years, for completion.

In a preliminary trial phosphorus pentoxide was distilled into bulb *m* in the way previously described. The bulb was then evacuated, the delivery tube sealed off, the apparatus inverted, and the septum  $S_3$  broken by means of the breaker in tube *l*. The apparatus was again set upright; the large hole in the septum was thus freed, this being necessary for the drying to take place as rapidly as possible in the given circumstances. As we feared, the drying of the solid substance was exceedingly slow, the effect after months being inappreciable. Finally we tried once more to prepare



the intensively dried, low-melting, asbestos-like form from the intensively dried, ice-like form, but obtained the high-melting form.

*The High-melting, Asbestos-like Form.*

*The Intensively Dried, High-melting, Asbestos-like Form* (First part).—The apparatus for determining the vapour pressure of this form was filled in the way described in our first publication (*loc. cit.*), a bulb, containing pure sulphur trioxide, of the form shown in Fig. 2 being used. The storing apparatus having been filled with the intensively dried ice form (see Fig. 2, *loc. cit.*), the glass spring indicator was first filled with this form.

By distilling sulphur trioxide alternately from one vessel into another, the distilling vessel being at room temperature or slowly heated and the condensing vessel cooled in liquid air, it is possible to convert the ice form almost completely into the high-melting, asbestos-like form; the last traces of the ice form are removed by distilling into one of the tubes and sealing it off.

As shown in our first publication, the dried ice form of sulphur trioxide, as in the case of a mixture, exhibits a lower vapour pressure after a small portion has been distilled off. This phenomenon, first observed with violet phosphorus ("Theory of Allotropy," pp. 96, 213), is exhibited in a much higher degree by the high-melting, asbestos-like form. The intensively dried, high-melting, asbestos-like form, obtained in the way mentioned above, showed a very low vapour pressure, which remained constant at room temperature. At higher temperatures, however, the vapour pressure rises with a velocity which decreases with the time. The apparatus being kept at constant temperature, this phenomenon has been studied successively with the same filling at 30° and 40°, and with a new filling at 50°; the results are shown in Figs. 5, 6, and 7. In these figures the curves approach asymptotically a final value, indicated by a dotted line.

Calculating  $T \ln p$  from the final values of the vapour pressure at the three temperatures, we obtain the results shown in Table III.

TABLE III.

$t$ .	$p$ (mm. Hg).	$T \ln p$ .	$Q/R$ .
30°	120	1450	8246
40	290	1780	8236
50	650	2090	8246

The three points obtained by plotting  $T \ln p$  against  $T$  are collinear as shown in the lower line of Fig. 8.

The behaviour of the high-melting, asbestos-like form agrees completely with that of the ice-like form. There are only quanti-

tative differences, due to the higher temperatures at which the high-melting asbestos-like form had to be studied. The velocity of establishment of inner equilibrium in the intensively dried material being

FIG. 5.

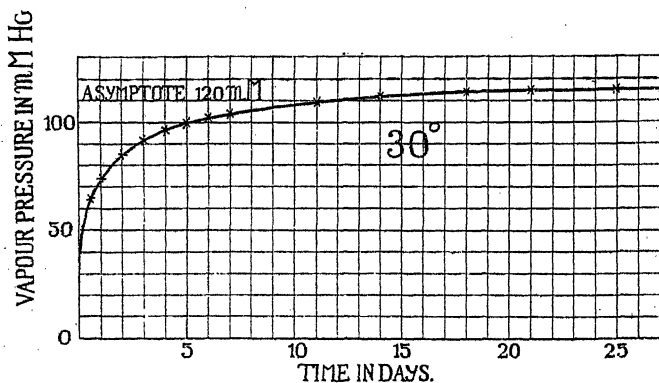


FIG. 6.

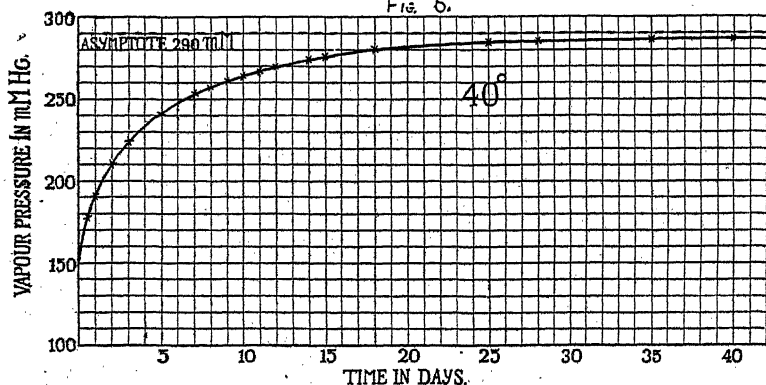
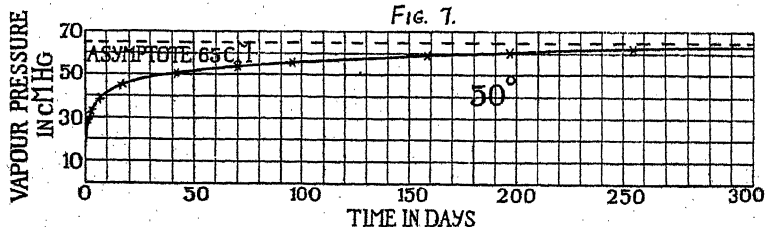


FIG. 7.

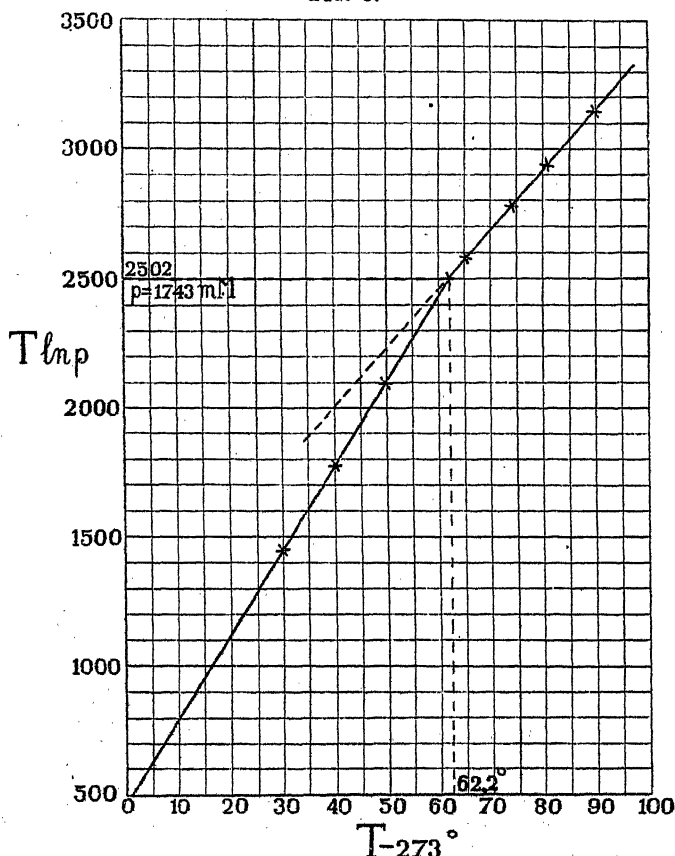


imperceptibly slow at 18°, the initial preparation, highly disturbed by rapid evaporation, showed an abnormally low vapour pressure, which did not change. At higher temperatures, however, the

velocity becomes greater and is manifested in the vapour pressure, which increases until inner equilibrium is reached. Violet phosphorus shows exactly the same interesting behaviour (*Z. physikal. Chem.*, 1916, 91, 249).

From the vapour-pressure curves of the high-melting form, in inner equilibrium, and of the liquid (Table I), we can find the unary

FIG. 8.



melting point of the high-melting, asbestos-like form under its own vapour pressure, i.e., the triple point  $S + L + G$  of this form. The two lines obtained by plotting  $T \ln p$  against  $T$  for the solid and the liquid form (Fig. 8) intersect at  $t = 62.2^{\circ}$  and  $T \ln p = 2502$ , or  $p = 174.3$  cm. of mercury.

As in the case of the ice-like form and the low-melting, asbestos-like form, we can calculate here the heat quantities. Thus, using

Q Q

the relationship  $T \ln p = -Q/R + CT$ , we find  $C = 32.0$ . The mean value of  $Q/R$  for the three observation temperatures (see Table III) is 8240, so that  $Q_{\text{sg}} = 16300$  cal. Now we know that  $Q_{\text{lg}} = 10100$  cal. Hence  $Q_{\text{sl}} = 6200$  cal. We see that the molecular heat of sublimation and the molecular latent heat of fusion are greatest with the high-melting, asbestos-like form, which seems to be most complex.

*The High-melting, Asbestos-like Form, dried only by Distillation.*—Before continuing the description of our experiments with the intensively dried, high-melting, asbestos-like form, we wish to state here that, starting with the not intensively dried, metastable, ice-like form, freshly distilled from a bulb of pure sulphur trioxide, and carrying out the experiment in the way described above, but in an apparatus without phosphorus pentoxide, we have easily obtained the stable, high-melting, asbestos-like form dried only by distillation.

We have examined this form to see if we could determine directly the unary vapour-pressure line of the high-melting, asbestos-like form. This proved to be impossible, for the substance behaved almost exactly like that intensively dried by phosphorus pentoxide. As is mentioned in our first paper on this subject, the literature states that the substance we call the high-melting, asbestos-like form, not intensively dried, shows a very slowly rising vapour pressure. Now, as this substance was of course separated from the ice-like form by distilling off the latter, it was likely that this distillation process was sufficient to lead to the very dry state necessary for the existence of the high-melting, asbestos-like form. Our method of transforming the ice-like form into the high-melting, asbestos-like form is a distillation process repeated several times and therefore it was to be expected that our preparation would be extremely dry.

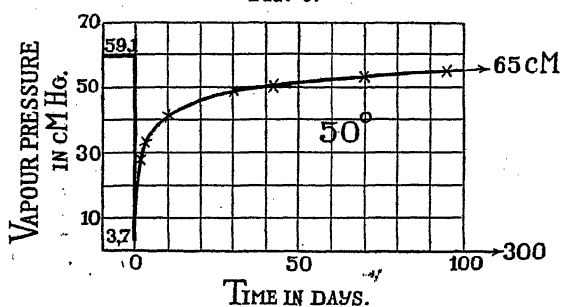
*The Intensively Dried, High-melting, Asbestos-like Form* (Second part).—We have already mentioned that in preparing the intensively dried, high-melting, asbestos-like form the last traces of all other forms are distilled off. In this process a part of the high-melting, asbestos-like form is evaporated also and the result is a high-melting, asbestos-like form of very low vapour pressure, constant at the ordinary temperature but rising perceptibly at temperatures above  $30^\circ$ .

We have studied this phenomenon more closely. In an apparatus filled with the intensively dried, high-melting, asbestos-like form which had stood some weeks in a thermostat at  $50^\circ$  the vapour pressure had risen to 591 mm. Hg., and was still rising very slowly. A part of the high-melting, asbestos-like form was now distilled off by cooling one of the condensing tubes in liquid air. After this tube

had been sealed off, and the apparatus replaced in the thermostat, the vapour pressure was found to have decreased enormously, namely, from 591 mm. to 37 mm. Hg. The vapour pressure, however, rose and readings made at intervals gave results which are represented graphically in Fig. 9.

The vapour pressure has risen above the initial pressure, in agreement with the fact that at the start the vapour pressure was still rising, although very slowly. The fact that the vapour pressure decreases so greatly on partial distillation proves that the high-melting asbestos-like form behaves as a mixed crystal consisting of at least two components differing largely in vapour pressure. These components must be pseudo-components, since after partial distillation the vapour pressure is not constant but rises, proving

FIG. 9.



that a more volatile part is formed from a less volatile part. Consequently the state for which the vapour pressure is abnormally low is a disturbed state of the stable, solid aggregation of the sulphur trioxide system.

As mentioned already, the unary melting point of the high-melting, asbestos-like form under its own vapour pressure is  $62.2^\circ$ , the pressure being 174.3 cm. Hg. Since it is possible to obtain different states of this high-melting asbestos-like form with very low vapour pressure it was important to determine the temperatures at which melting occurred. Since the glass spring is apt to be broken by a sudden rise of vapour pressure, the experiments were carried out very carefully, the temperature of the thermostat being raised slowly and continuously, so that each experiment lasted 2 or 4 days. Although this slow working is not favourable for producing the largest effect, the results in Table IV were obtained.

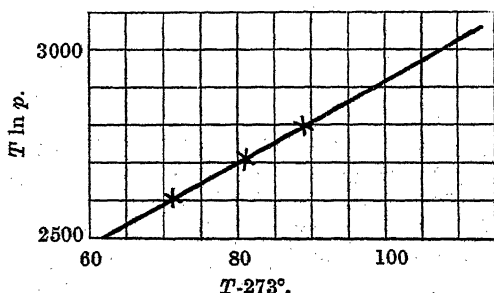
Thus the initial melting points lie respectively  $9^\circ$ ,  $19^\circ$  and  $26.5^\circ$  above the unary melting point of the high-melting, asbestos-like form under its own vapour pressure. With more rapid working it should not be difficult to realise still higher initial melting points.

TABLE IV.

Preparation.	Initial m. p.	Vap. press. (cm. Hg) at initial m. p.	$T \ln p.$	Vap. press. (cm. Hg) of the liquid if in inner equilibrium.
I.	71.0°	192	2601	266.0
II.	81.0	212	2711	400.2
III.	88.8	227	2796	642.7

A very remarkable phenomenon is that as soon as melting begins the vapour pressure rises so rapidly that it is very difficult to prevent the glass spring from being broken. This phenomenon had been expected, for we had already observed that, although the intensively dried liquid phase could behave as a mixture at relative low temperatures, at higher temperatures, *e.g.*, above 50°, the establishment of the inner equilibrium in the liquid took place rapidly. According to the theory of allotropy the liquid initially produced by the melting of a disturbed state of the high-melting, asbestos-like

FIG. 10.



form with a very low vapour pressure, due to the low concentration of the volatile pseudo-components, is a liquid, co-existing with this disturbed solid state, also having an abnormally low vapour pressure, since it contains little of the more volatile pseudo-component. Now, whilst the velocity of establishment of inner equilibrium in the solid, intensively dried, high-melting, asbestos-like form is slow even at, *e.g.*, 81°, inner equilibrium will be established with great rapidity in the liquid. For this state, the vapour pressure at 81° is 400.2 cm. Hg (value calculated by interpolation), so that, when melting begins at 81°, at a vapour pressure of 212 cm. Hg, the vapour pressure must rise considerably at constant temperature.

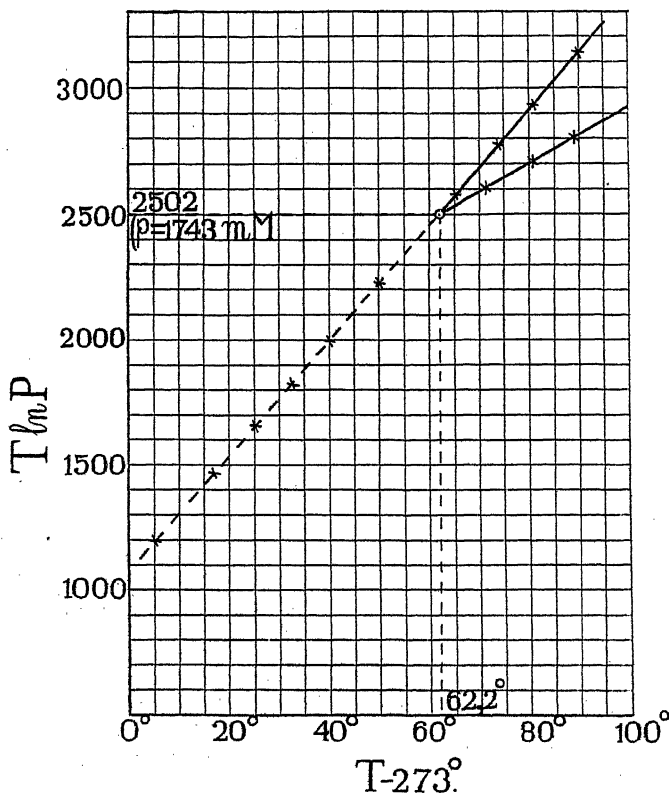
The determination of the temperature and pressure at which the disturbed solid state under consideration begins to melt is very important, for it is evident that these points, where a disturbed solid state co-exists with liquid and vapour (also not in inner equilibrium), are points on a three-phase line in the pseudo-system.

Though the equation  $d \ln p/dT = Q/RT^2$  does not hold for a

three-phase equilibrium, the curve of  $T \ln p$  plotted against  $T$  is a straight line, as Fig. 10 shows.

As is demonstrated in detail in the "Theory of Allotropy" (p. 18, Fig. 24; p. 28, Fig. 41), the unary melting point under vapour pressure is situated where the unary vapour pressure curve, *i.e.*, the vapour pressure curve of the liquid phase in inner equilibrium, meets a three-phase line for the co-existing solid, liquid, and vapour.

FIG. 11.



Plotting  $T \ln p$  against  $T$  both for the three-phase system and for the unary liquid system we obtain Fig. 11, showing the intersection of these lines at  $62.25^\circ$  and  $174.3$  cm. Hg. This is in complete agreement with our experiments mentioned on p. 1115.

*Initial Melting Points of the Highly Disturbed States of the High-melting, Asbestos-like Form.*

In the vapour pressure determinations of the disturbed states of the high-melting, asbestos-like form the rate of heating was very

slow, especially at higher temperatures, in order to prevent the glass spring from being broken. To ascertain at what temperatures melting would occur if the disturbed substance was heated less slowly, some tubes were filled with the intensively dried, high-melting, asbestos-like form, disturbed as much as possible by partial distillation, in the same way as was done in our vapour-pressure apparatus. After being sealed off, these tubes were placed in a stirred oil-bath, the temperature of which was slowly raised. The temperatures at which melting began are in Table V.

TABLE V.

Tube.	Initial m. p.	Vap. press. (cm.) at the moment melting began.	Vap. press. (cm.) of the liquid in inner equilibrium.
I.	65.0°	179.1	198.7
II.	77.0	203.7	344.7
III.	95.0	238.8	703.6

It is seen that initial melting points are realised up to 33° above the melting point of the same substance if in inner equilibrium. These experiments were dangerous, since, as has already been mentioned, the liquid formed establishes inner equilibrium and the pressure rises suddenly to relatively high values.

To demonstrate this we have inserted columns three and four in Table V. The third column shows the pressure at the moment the liquid is formed (the pressure on the three-phase line at the temperature considered here), and the fourth column shows the pressures reached when the liquid formed has established inner equilibrium. In the last case, the pressure rises from 3.14 atm. to 9.24 atm. Obviously the increase of vapour pressure takes place very rapidly and in fact caused a very serious explosion on one occasion.

#### *The Position of the Unary System in the Pseudo-system.*

In our first paper on this subject (*loc. cit.*) and in the previous pages of this paper we have described the investigations leading to our knowledge of the  $P$ - $T$  diagram of the unary system sulphur trioxide with regard to the equilibria in the vapour phases.

The schematical diagram is shown in Fig. 12.

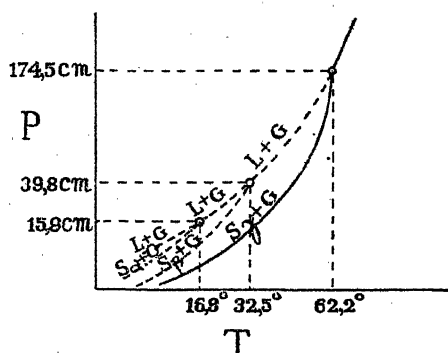
Further it has proved that the intensively dried phases of sulphur trioxide behave like the phases of a mixture. The continuous change in the vapour pressure of the ice-like form caused by distillation enabled the region of the pseudo-system, to which this form belongs, to be studied. It is the region of a dissociable compound, forming mixed crystals which, if behaving as a unary substance, are a little richer in the more volatile pseudo-component than is the ordinary compound.



As regards the high-melting, asbestos-like form, this stable modification exhibits the phenomenon of falling vapour pressure on partial distillation even more strongly than the ice-like form, and by studying the states of different vapour pressure we found another part of the pseudo-system, namely, that to which the high-melting, asbestos-like form belongs. We realised also a part of a three-phase line for co-existing vapour-liquid-solid, the last phase of which is a mixed crystal of variable composition.

The unary, high-melting, asbestos-like modification is a mixed crystal of the same pseudo-components, with this peculiarity, that the pseudo-components are in inner equilibrium.

FIG. 12.



$S_{\alpha}$  = ice-like form;  $S_{\beta}$  = low-melting, asbestos-like form;  $S_{\gamma}$  = high melting, asbestos-like form.

As to the ice-like form, we were fortunate enough to be able to study the larger part of the three-phase line of this form, from which the conclusion could be drawn that the solid co-existing phase was a compound.

The three-phase line of the high-melting, asbestos-like form could only be studied to a small extent, and so far we do not know whether this form is a mixed crystal of a compound or a mixed crystal of the high-melting pseudo-component. For the present, this does not matter, and we will assume here the latter simple case.

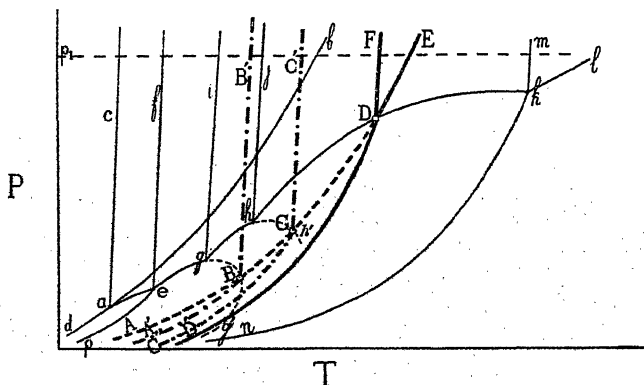
The low-melting, asbestos-like form, which, as already stated, is easily obtained so long as the sulphur trioxide has not been intensively dried, does not appear or appears only in very small quantity if this has been intensively dried. The three-phase line to which the unary melting point under its own vapour pressure, i.e., the triple point, of this form belongs therefore cannot be studied until this form, prepared in the not intensively dried state, is intensively dried. This drying will take several years and therefore we

cannot say whether the low-melting, asbestos-like form is a mixed crystal of a compound or a mixed crystal of a second series of mixed crystals of the highest-melting pseudo-component.

Though the answer to this question will be very interesting, it can have very little influence on the pseudo-system and the situation of the unary system in it which can be deduced from our observations.

In one or two reviews of "The Theory of Allotropy" appears the criticism that the phenomenon of allotropy is regarded as being very complicated. Now it is most remarkable that by chance the first system that could be studied more closely, thanks to the ease of drying, not only gives a strong confirmation of the theory but also shows that the pseudo-system of the so-called simple substance sulphur trioxide is much more complex than the most complicated case dealt with in the theory mentioned above.

FIG. 13.



We will start with the  $P$ - $T$  diagram (Fig. 13). It is the diagram of a system of two pseudo-components in which two dissociable compounds appear. The minimum melting points of the compounds, however, are metastable, since the three-phase lines intersect at pressures situated above them.

The case we have to consider here is not one of the simple cases dealt with in the "Theory of Allotropy" (pp. 28, 34), but the much more complicated one following from these cases if compounds are formed.

$a$  is the triple point of the pseudo-component  $\alpha$ , and  $k$  is the triple point of the pseudo-component  $\beta$ . These points are connected by four three-phase lines,  $ae$  representing the three-phase line for the co-existing system  $\alpha$ -mixed crystals + liquid + vapour;  $egg'$  the three-phase line for the co-existing system  $\alpha\beta$ -mixed crystals + liquid + vapour;  $ghh'$  the three-phase line for the co-existing system

$\alpha\beta$ -mixed crystals + liquid + vapour; and  $hk$  the three-phase line for the co-existing system  $\beta$ -mixed crystals + liquid + vapour. We see that the greater part of the three-phase line  $ghh'$  represents metastable states.

The position of the unary system in this pseudo-system is given by thick lines. The line ABCDE is the vapour-pressure curve for the liquid in inner equilibrium. Where this curve meets a three-phase line of the pseudo-system a three-phase co-existence of the unary system appears. Every one of the three phases is in inner equilibrium or, in other words, there appears a unary melting point under its own vapour pressure (a unary triple point). The first meeting takes place at D, the stable unary melting point under its own vapour pressure. Further, the metastable part of the unary vapour-pressure line of the liquid still meets two metastable three-phase lines, one at C and the other at B. These points are metastable unary melting points under vapour pressure. At every unary melting point under vapour pressure, or triple point, three two-phase lines meet. The stable sublimation curve, D'D, the stable vapour-pressure curve of the liquid, DE, and the stable melting curve, DF, meet in the stable triple point and the three curves which meet at the two metastable triple points C and B are metastable.

This figure now represents substantially the  $P$ - $T$  diagram of the pseudo-system of sulphur trioxide and the position of the unary system in that pseudo-system. ABCDE is the vapour-pressure line of liquid sulphur trioxide in inner equilibrium. A'B is the vapour pressure line of the ice-like form in inner equilibrium, and the three-phase line  $egBg'$  that of the pseudo-system, which is a three-phase line for the co-existence of mixed crystals of a compound-liquid-vapour. C'C is the vapour pressure line of the low-melting asbestos-like form in inner equilibrium, and the three-phase line  $ghGh'$  that of a mixed crystal of a compound + liquid + vapour, but it is also possible that instead of a mixed crystal of a compound, series of mixed crystals of the  $\beta$ -pseudo-component are existing—which, however, does not change our diagram.

D'D is the vapour pressure line of the high-melting, asbestos-like form in inner equilibrium, and  $hDk$  is a three-phase line of the pseudo-system for the co-existing system mixed crystals of the  $\beta$ -pseudo-component + liquid + vapour.

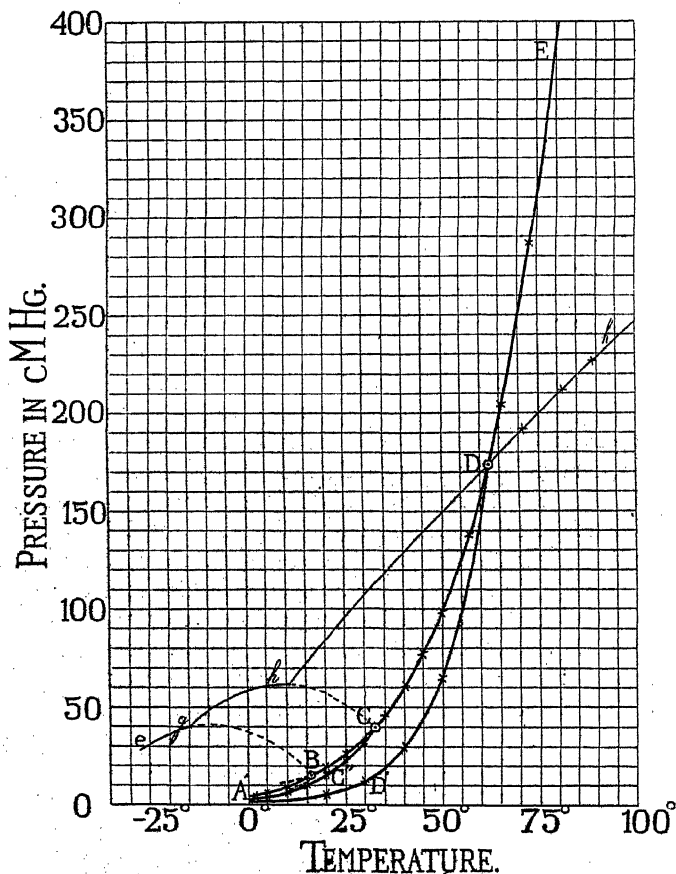
It is possible that here, instead of mixed crystals of the  $\beta$ -pseudo-component, mixed crystals of another compound are co-existing, but as we do not know this, we will assume here the simplest case. Moreover, for an insight into the connexion of the pseudo- and unary systems this question is of little importance.

At two places now we have been able to penetrate the pseudo-

system, (1) in the region to which the ice-like form belongs, and (2) in the region to which the high-melting, asbestos-like form belongs.

By distilling off the intensively dried, ice-like form compositions different from that of the unary ice-like form could be obtained and so it was possible to determine a part of the three-phase line  $egBg'$ .

FIG. 14.



By distilling off the intensively dried, high-melting, asbestos-like form, enormously high effects were realised and states were obtained the vapour pressures of which were reduced up to  $1/15$  of the vapour pressure at inner equilibrium at the same temperature. In this connexion vapour-pressure lines could be realised lying far below the unary vapour-pressure line  $D'D$ .

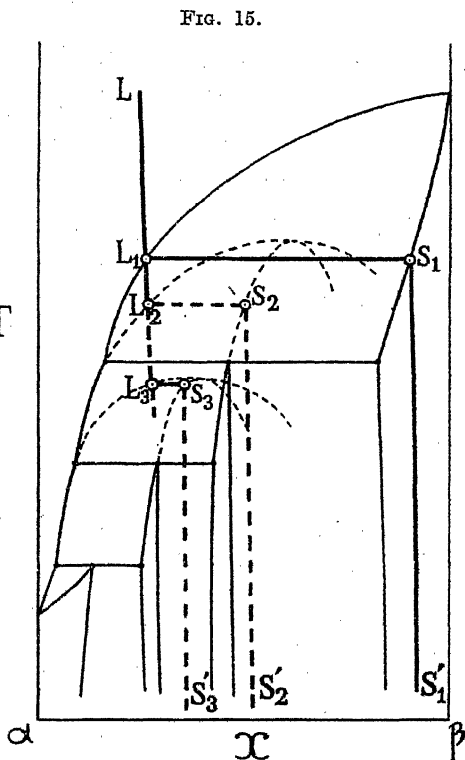
This phenomenon enabled us, by continuing these curves, to

determine a part of the three-phase line  $kDk$  of the pseudo-system. Thus the curve  $Dk$  could be determined over a range of about  $30^\circ$ . The  $P$ - $T$  diagram considered here is a diagrammatic one. Drawing the observed curves of the most interesting part just as they have been found, we get the  $P$ - $T$  diagram in Fig. 14.

Finally we give diagrammatically the melting-point figure (Fig. 15) corresponding with the constant pressure indicated in the  $P$ - $T$  diagram (Fig. 13) by  $p_1$ .

Reference to the "Theory of Allotropy" (p. 36) will render this melting-point figure comprehensible at once.

In connexion with our  $P$ - $T$  diagram two compounds appear giving mixed crystals. The melting points of these compounds are situated in metastable regions. The line  $LL_1L_2L_3$  specifies the inner equilibria in the liquid at different temperatures. Where this line meets a melting-point curve of the pseudo-system a unary melting point appears. Three such meetings take place, one at  $L_1$ , a second at  $L_2$ , and a third at  $L_3$ . The co-existing phases at the unary stable melting equilibrium, indicated



by the liquid phase  $L_1$  and the solid phase  $S_1$ , represent the melting equilibrium of the high-melting, asbestos-like form.\* Similarly,  $L_2$  and  $S_2$  indicate the metastable co-existing phases of the low-melting, asbestos-like form at the metastable unary melting equilibrium, and  $L_3$  and  $S_3$  represent the same for the ice-like form. The lines  $S_1S_1'$ ,  $S_2S_2'$ , and  $S_3S_3'$  specify the inner equilibria of the

\* We prefer here to speak of melting equilibrium and not melting point, since in the  $T$ - $X$  diagram the melting phenomenon is indicated by two points, one representing the solid and the other the liquid phase.

stable and of the two metastable solid states at different temperatures, under constant pressure. Our  $P$ - $T$  and  $T$ - $X$  diagrams do not show a eutectic, which is most probable if  $\beta$  is a polymeride of  $\alpha$ .

It appears from our study of sulphur trioxide that the "Theory of Allotropy" has not represented the phenomenon as more complicated than it is. From the experiments of H. B. Baker and Mrs. Baker as well as our own, it was to be expected that a study of substances in an intensively dried state would offer the greatest chance of finding out something about the complexity of the so-called simple substances and we have found that the two first substances which could be obtained easily in an intensively dried state, namely, sulphur trioxide and phosphorus pentoxide, showed the complexity in a most distinct way.

Nature is very complex; and the old theory of allotropy is not satisfactory, for it cannot be assumed that we have studied accidentally the only substances showing complexity. We have studied the substances most easily dried, and we may expect that other substances in the intensively dried state will also show complexity, for there is little doubt that complexity is a general phenomenon.

In the next paper we shall deal with the results of our X-ray investigations.

#### *Summary.*

The investigation of the ice-like form of sulphur trioxide has been completed. The unary sublimation curve and the unary vapour-pressure line of the liquid having been determined, the heat quantities can be calculated. The unary triple point is at  $16.8^\circ$  and 158.5 mm. Hg.

The low-melting, asbestos-like form has been studied in the not intensively dried state, in which it is in inner equilibrium, so that here also the heat quantities can be calculated. The unary triple point of this form is at  $32.5^\circ$  and 398 mm. Hg.

The intensively dried, low-melting asbestos-like form cannot be prepared from the intensively dried, ice-like form; instead of the low-, the high-melting form always appears. The intensive drying of the low-melting asbestos-like form must be done with the substance in the solid state, and will take perhaps several years.

The high-melting, asbestos-like form has been studied closely in the intensively dried state. It exhibits more strongly than any other form the property of diminishing vapour pressure on distillation. A decrease from 59.1 to 3.7 cm. Hg has been observed.

The abnormally low vapour pressures remain constant at room temperature. But at higher temperatures the vapour pressure increases with a velocity which decreases with the time. This proves the velocity of the establishment of the inner equilibrium

to be imperceptibly slow at  $18^{\circ}$ . At higher temperatures, however, this velocity increases, and becomes manifest in the increasing vapour pressure, until inner equilibrium is reached. The vapour tensions asymptotically approach final values, being the values corresponding to inner equilibrium. The unary sublimation curve of this form has thus been found and the heat quantities have been calculated. The unary triple point of this form is at  $62.2^{\circ}$  and 174.3 cm. Hg.

In a second section the intensively dried, high-melting asbestos-like form has been considered more closely, and the phenomenon of diminishing vapour pressure on distillation studied in detail. The initial melting points (and the corresponding vapour pressures) of states of different low vapour-pressures lie up to  $33^{\circ}$  above the melting point of the same substance if in inner equilibrium.

The observed phenomena prove that the high-melting asbestos-like form is a mixed crystal of at least two pseudo-components differing widely in volatility and melting point.

Application of the theory of allotropy to these results enables the position of the unary system in the pseudo-system to be deduced. This position is given in a  $P$ - $T$  diagram and in a  $T$ - $X$  diagram and by its means the observed phenomena can easily be demonstrated.

This study shows most clearly that nature is very complex, and the old simple theory, being unsatisfactory, is to be replaced by the theory of allotropy.

THE UNIVERSITY, AMSTERDAM.

[Received, January 21st, 1926.]

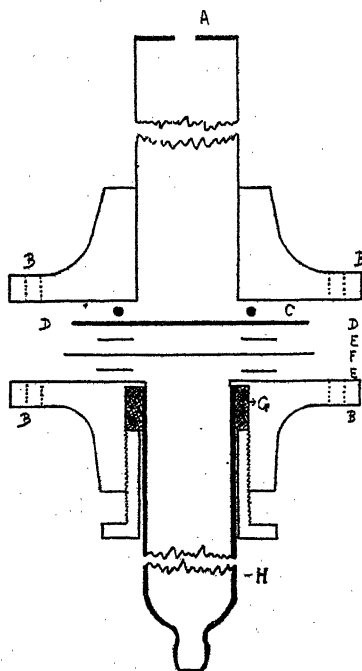
## CXLVI.—*Preparation of Nickel Membranes for Ultrafiltration.*

By JOHN MANNING.

THE membranes which have hitherto been used for ultrafiltration have usually been prepared by impregnating filter-papers with nitrocellulose dissolved in acetic acid or in a mixture of ether and alcohol. They can neither be used at high temperatures nor with solvents such as acetone. In this communication are described membranes, prepared by the electrical deposition of nickel on fine nickel gauze, which can be used at high temperatures and in the presence of organic solvents.

The apparatus shown in the figure is made of nickel-plated phosphor-bronze. The two flanges are bolted together with the membrane between. The membrane alone could not stand the

high pressure involved and was therefore supported by a nickel disc through which several holes had been drilled. Various materials were tried as washers, but the most suitable was a pure silver-wire ring softened by annealing. This was flattened between the flanges when they were screwed together and made a very satisfactory joint. The apparatus could be used with pressures up to sixteen atmospheres.



*Ultrafilter.*  
A Screw for pressure gauge. B Holes for  $4\frac{3}{8}$ " bolts. C Silver ring. D Membrane. E Silver washers. F Perforated nickel support for membrane. G Asbestos compressed against glass tube. H Thick glass tube.

As a foundation for the membrane, fine nickel gauze (mesh 200) and, in later experiments, phosphor-bronze gauze was used.

In the early work, a nickel sheet of suitable size was made the anode in a solution which was agitated by using the cathode itself as a vertical stirrer. The solutions were similar to those used for ordinary nickel-plating, containing, for example, 120 g. of nickel sulphate, 22.5 g. of ammonium chloride, and 15 g. of boric acid per litre. With the current densities first used, smooth, even, and hard deposits were obtained, perforated with small holes. If the plating process was continued until these were filled in, the rest of the membrane became entirely impermeable. With high current densities, *i.e.*, 2 amps. per 4 sq. in., at 3.3 volts very irregular deposits were obtained. As the current density and *E.M.F.*

were decreased, the character of the deposit changed; it became less hard and darkened in colour and, at 0.3—0.5 amp. per 4 sq. in. at 0.9—1.1 volts, the resulting membranes were almost black and fairly regular. The suitability of the above membranes for ultra-filtration was tested by means of the following experiments.

A colloidal solution of silver in stearic acid, prepared by the reduction of silver stearate suspended in the acid (Giles and Salmon, *J.*, 1923, 123, 1600), was filtered at 140° under a pressure of 2 atmospheres. Perfectly clear stearic acid came through, the colloidal



metal being entirely retained as a blue deposit on the membrane. A second experiment was carried out with a solution in which only partial reduction had taken place, so that there was present a considerable excess of silver stearate. In this case, silver was found in the filtrate, which was colourless, showing that, although the colloidal metal had been retained, the silver stearate, which we believe to exist as simple molecules, passed through the membrane.

These membranes would also successfully filter arsenic sulphide and ferric hydroxide hydrosols, but they were not satisfactory with solvated organic colloids, such as gelatin in water, or nitro-cellulose in ether and alcohol. It seemed probable that filtration was taking place through a small number of holes, whilst the rest of the membrane was practically solid. These holes, which would retain inorganic solids and permit the passage of the solvent, became rapidly blocked up with gelatin. It was therefore necessary to obtain a more porous and open deposit, and experiments were carried out to determine the effect of changes in the composition of the plating bath on the character of the deposit.

The presence of nickel chloride is usually considered to give a soft deposit; consequently, membranes were prepared by plating in solutions of that salt (100 g. of nickel chloride, 20 c.c. of concentrated hydrochloric acid, and 1500 c.c. of water), hydrochloric acid being added to give a continuous evolution of gas at the cathode and thus increase the porosity of the deposit. At low current densities, the membranes were more smooth and even than with higher current densities, but contained green patches due to the high concentration of chlorine ions present; consequently, in later experiments, sulphuric acid was used instead of hydrochloric acid, and nickel sulphate was substituted for a part of the chloride. Table I shows the effect of varying the relative proportion of chloride and sulphate in the plating bath, the most effective membranes being obtained when the ratio of sulphate to chloride was 50 to 80.

The effect of varying the hydrogen-ion concentration on the nature of the membrane was also investigated. In one experiment, boric acid was used instead of sulphuric acid, in the hope that it would act as a hydrogen-ion regulator. Deposits in this case were hard with bright streaks and not efficient for filtration. In later experiments, the following plating mixture was used: 100 g. of nickel sulphate, 80 g. of nickel chloride, 20 g. of sodium acetate ( $3\text{H}_2\text{O}$ ), and 1500 g. of water. The membranes which were obtained were suitable for ultrafiltration and were much less brittle than those prepared from previous solutions. With a still larger proportion of acetate the membranes became greenish and

TABLE I.

The bath contained 1500 c.c. of water, 5 c.c. of concentrated sulphuric acid, and weights (g.) of nickel chloride and sulphate as indicated.

Current densities : 1.1 amps. down to 0.4 amp. per 4 sq. in. Potential difference : 3.5 volts for 1 hr. and 2 volts for about 18 hrs.

Bath.		Remarks on membranes.		
$\text{NiSO}_4$ .	$\text{NiCl}_2$ .	Appearance.	Thickness.	Filters
0	100	Black.	Flimsy.	Night blue.
20	100	Greenish.	Denser.	
40	80	"	"	Night blue and gelatin.
50*	80	Brown, sometimes greenish.	"	Night blue and cellulose acetate.
120	20	Irregular.		
120	0	No deposit from acidified solutions.		

\* The 3rd and 4th membranes prepared from this bath were much better than the first two. The bath was filtered and acidified with 5 c.c. of concentrated sulphuric acid before each successive plating operation.

still more pliable. In the next paragraph are described experiments carried out with these membranes.

*Ultrafiltration of Cellulose Acetate in Acetone and Water.*—Cellulose acetate was dried and dissolved in a mixture of acetone and water, the acetone having been purified by the method of Werner and Shipsey (J., 1913, 103, 1255). Solutions of known concentration were prepared in tightly-corked flasks and, to prevent evaporation, were transferred to the ultrafilter through glass tubing. The filtration of 3 to 5 c.c. took from 10—15 hrs. at a pressure of 10—14 atmospheres and, to avoid loss of acetone by evaporation, the filtrate was allowed to fall directly into a known weight of water. The acetone was estimated by Messenger's method (*Ber.*, 1888, 21, 3386). The results of three experiments are shown in Table II, the figures in the column "Cellulose acetate" showing the weight (g.) added to 100 g. of mixed acetone and water.

TABLE II.

Initial concentrations.			Concentrations after ultrafiltration.	
Cellulose acetate.	Acetone %.	Water %.	Acetone %.	Water % (by diff.).
3.25	74.9	25.1	75.5	24.5
5.41	68.0	32.0	68.3	31.7
3.73	71.1	28.9	71.7	28.3

The analytical error is about 1%.

The concentration of the acetone would be expected to fall on

account of its volatility, but, on the other hand, there appears to be a slight increase in concentration in the filtrate, indicating apparently that water is taken up by cellulose acetate (from these mixtures, at any rate) to a greater extent than acetone.

*Ultrafiltration of Sodium Stearate.*—Solutions of sodium stearate of concentrations lying between  $N/2$  and  $N/6$  were ultrafiltered at a temperature between  $80^{\circ}$  and  $90^{\circ}$ , the whole ultrafilter being surrounded by an electric oven. In every case, only a negligible amount of stearic acid penetrated the membrane, whilst the alkalinity of the filtrate was always less than  $0.01N$ , indicating that membrane hydrolysis had not taken place to any considerable extent.

Solutions of casein and gelatin were also successfully filtered by means of this membrane. In the case of  $0.5\%$  gelatin sols, extremely small quantities of gelatin passed through the filter at  $16^{\circ}$ , but, on raising the temperature to  $45^{\circ}$ , the gelatin almost entirely passed through. This means that the particles present at the higher temperature are too small to be retained. If we accept the view, which will be discussed in a later communication, that the difference between gelatin at these two temperatures is due to the secondary linking up of particles, then the primary particles of gelatin are considerably smaller than is usually believed.

*Determination of Size of Pores.*—One of Bechhold's methods for the determination of the size of pores depends on the minimum air pressure which will produce bubbles through the membrane covered 1 mm. deep with water.

Some irregularities in the membranes were detected by this method, one or two large holes usually being found. In a particular case, at a pressure of 3.5 atmospheres there was bubbling at one hole, at 4 atmospheres at 5 holes, and at 4.8 atmospheres the bubbling became general. In view of the results obtained, it seems probable that these large holes are very quickly blocked up during filtration. It was observed many times that initially the colloid came through, but was retained after the first few drops.

The finest membranes obtained contained pores of between  $50-80\ \mu$ , the size increasing as the nickel sulphate content of the plating bath increased, until the average size of the pores was  $300\ \mu$ , for a bath containing 90 g. of nickel sulphate, 80 g. of nickel chloride, 1500 g. of water, and 5 c.c. of concentrated sulphuric acid.

### *Summary.*

Membranes have been prepared by nickel plating on bronze or nickel gauze which are capable of retaining most colloids on ultrafiltration. They can be used at high temperatures, and with

solvents which will attack the usual membranes. The average size of the pores can be controlled by varying the plating bath, so that they can be used for fractional filtration.

The author is indebted to the Department of Scientific and Industrial Research for a grant which enabled the above work to be carried out, and also to Mr. C. S. Salmon, who suggested the subject and continually gave very valuable advice in the course of the experiments.

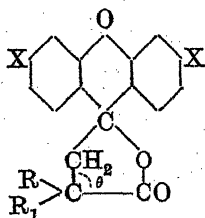
KING'S COLLEGE, LONDON.

[Received, January 29th, 1926.]

## CXLVII.—*Ring-chain Tautomerism. Part XV. The Phenol-succineins and -glutareins.*

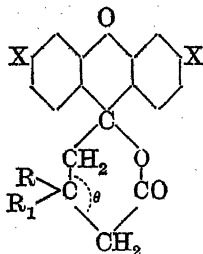
By SIKHIBHUSHAN DUTT.

IN a previous paper (Dutt and Thorpe, J., 1924, 125, 2524) it was shown that the effect of increasing complexity of the substituents R and R<sub>1</sub> in fluoresceins and rhodamines, derived from  $\alpha$ -disubstituted succinic and  $\beta\beta$ -disubstituted glutaric acids, of the following constitutions



Succinylfluoresceins; X = OH.

Succinylrhodamines; X = NMe<sub>2</sub>.

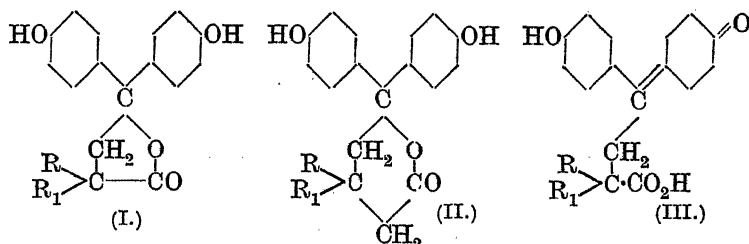


Glutarylfluoresceins; X = OH.

Glutarylrhodamines; X = NMe<sub>2</sub>.

is to diminish the tetrahedral angle ( $\theta$ ) between the directions of the two remaining valencies of the substituted carbon atom; the stability of the lactone ring is thereby progressively increased, and consequently the amount of open-chain coloured quinonoid derivative produced by the action of alkalis and acids on these compounds progressively diminishes. The results of that research, which were based on spectroscopic data, were in complete accord with the results obtained by Thorpe and his collaborators, working on the same problem from other points of view.

The phenolsuccineins (I) and phenolglutareins (II),

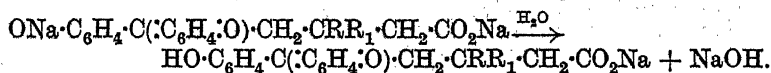


where  $RR_1$  represent HH, MeMe, MeEt, EtEt, and the *cyclohexane* residue, have now been prepared and their absorption maxima determined. The results obtained are in complete agreement with those found in the cases of the corresponding fluoresceins and rhodamines (*loc. cit.*) and thus serve to confirm the generalisation stated above.

Like phenolphthalein, the phenol-succineins and -glutareins described in this paper are all colourless, crystalline substances which dissolve in alkalis with a bright pink colour, the mechanism of transformation from the colourless (I) to the coloured form (III) being the same as in the cases of the fluoresceins and rhodamines, *viz.*, fission of the lactone ring and formation of a quinonoid substance. The red quinonoid form is stable only in alkaline solution, the stability being due to salt formation at the carboxyl group, and on acidification reverts to the original colourless lactone form.

Green and Perkin have shown (J., 1904, 85, 398) that the gradual disappearance of the deep pink colour produced by treating phenolphthalein with an excess of alkali is due to the formation of a carbinol salt,  $(ONa \cdot C_6H_4)_2C(OH) \cdot C_6H_4 \cdot CO_2Na$ , produced by hydration of the quinonoid form,  $ONa \cdot C_6H_4 \cdot C(C_6H_4 \cdot O) \cdot C_6H_4 \cdot CO_2Na$ . On acidifying the colourless solution of the carbinol salt, the free carbinol is obtained, which spontaneously loses water and is reconverted into the original lactone.

In presence of alkali, the phenolsuccineins and, very much more rapidly, the phenolglutareins undergo changes similar to the above, only a slight excess of alkali being necessary to produce them. In fact, the normal red quinonoid salts of the phenolglutareins are unstable in solution even in the absence of an excess of alkali. These salts, which have an alkaline reaction in solution, probably dissociate into the monoalkali salts and alkali hydroxide:



The liberated alkali then brings about hydration at the quinonoid linking, the carbinol derivatives being formed. The red quinonoid forms, however, are more stable in very dilute solution.

The *carbinol* derivative of phenolglutarein,



has been isolated as a colourless, crystalline substance. It is stable under ordinary conditions, but is converted into the lactone by the action of heat or dehydrating agents, such as concentrated hydrochloric or sulphuric acid, anhydrous zinc or aluminium chloride, and stannic chloride. The *carbinol* derivative of phenol- $\beta$ -methylglutarein is very unstable and, although capable of isolation, passes into the lactone in the course of a few minutes. No carbinol derivative could be isolated from any of the remaining phenol-succineins or -glutareins.

The rate of hydration of the phenolglutareins under the influence of alkali, the end-point being where the red solution became colourless, was, under exactly similar conditions, slowest in the case of phenolglutarein, and progressively increased with the complexity of the substituents in the glutaric acid residue.

From the table (p. 1139) showing the relative rates of hydration of the various phenolglutareins in different concentrations of alkali, it will be seen that in dilute solution the rate is almost unaffected by the concentration of the alkali, thus proving that the change is a unimolecular one. The hydration of the phenolsuccineins was so slow and irregular that trustworthy measurements could not be made.

Stannic chloride is the only agent that has been found to bring about the condensation of phenol with succinic and glutaric acids and their substituted derivatives in the desired direction and in a satisfactory manner; with fused zinc chloride and with hydrogen chloride, the yields obtained are practically valueless. Strong sulphuric acid and phosphorus oxychloride produce the diphenyl esters of these acids, and anhydrous aluminium chloride produces complex pyrone derivatives which are probably similar in constitution to *o*-phenolphthalein anhydride.

#### EXPERIMENTAL.

*Phenolsuccinein*.—The preparation of this compound is attended with difficulty on account of the ease with which it becomes hydrated to the carbinol derivative and subsequently further decomposed into simpler substances. Dilute alkalis effect this change very quickly; even long contact with water, dilute alcohol, or dilute acids brings about the same transformation. The effect is quickened

by heating. But once the compound has been isolated and dried, the rate of hydration becomes very much slower. After a trial of various methods the following was adopted for the preparation of this compound :

A mixture of 12 g. of succinic acid, 25 g. of phenol, and 13 c.c. of stannic chloride was heated on the steam-bath for 4 hours, the melt treated with pure dry ether, and the insoluble salmon-coloured crystalline compound filtered off and washed with absolute alcohol-ligroin (1 : 3 by vol.). The almost colourless residue, containing tin salts, was dissolved in cold absolute alcohol, dry hydrogen sulphide passed through the solution, the excess of the gas removed by carbon dioxide, and the filtered solution concentrated in a vacuum at the ordinary temperature; addition of light petroleum then precipitated *phenolsuccinein* in colourless needles. This compound and the succeeding ones are described in the tables.

*Phenol-as-dimethylsuccinein*.—A mixture of *as*-dimethylsuccinic acid (1 mol.), phenol (2 mols. plus 20% excess), and stannic chloride (1 mol. plus 20% excess) was heated on the steam-bath for 4 hours, the melt poured into water, and the excess of phenol distilled in steam; the condensation product solidified, on cooling, to a mass of crystals in a matrix of brittle, dark brown, resinous matter. The latter was removed by washing the finely-powdered product with absolute alcohol-ligroin (b. p. 70—80°); the almost colourless crystalline residue recrystallised from alcohol (animal charcoal) in long, colourless, silky needles.

Phenolsuccineins were obtained from *as*-methylethyl-, *as*-diethyl-, and *as*-cyclohexane-succinic acids by exactly similar methods.

*Phenolglutarein*.—The rapid hydration of this compound and subsequent decomposition into simpler substances make its preparation exceedingly difficult.

The *lactone form* was obtained from a mixture of glutaric acid (13 g.), phenol (25 g.), and stannic chloride (13 c.c.) by the method for preparing phenolsuccinein. It crystallised from absolute alcohol-ligroin in colourless, silky needles.

*Quinonoid form*. The ethereal filtrate in the preceding preparation was shaken with concentrated hydrochloric acid to remove tin salts, the ether distilled off, and the residue, after addition of an equal volume of 50% sulphuric acid, distilled in steam until phenol ceased to pass over. The red, sticky substance in the distilling flask was extracted with ether, the ethereal solution dried, diluted with ligroin, and allowed to evaporate at the ordinary temperature. After a month, the gummy residue had partly solidified, with separation of small crystals. These were spread

on a porous plate, washed free from the sticky mother-liquor with absolute alcohol-ligroin (1:4 by vol.), and recrystallised from ether; glistening, red prisms were thus obtained which, on heating, decomposed without melting. The substance changed into the colourless lactone form after contact with concentrated hydrochloric acid for several days or when its solution in concentrated sulphuric acid was poured into ice-cold water (Found: C, 71.5; H, 5.8.  $C_{17}H_{16}O_4$  requires C, 71.3; H, 5.7%).

*Carbinol form.* The sticky mother-liquor was extracted from the porous plate by sodium carbonate solution, in which it dissolved with a bluish-red colour, but the solution soon became colourless. On acidification, a colourless solid was precipitated which crystallised from dilute alcohol in glistening, white needles, m. p.  $220^{\circ}$  (Found: C, 67.3; H, 5.8.  $C_{17}H_{18}O_5$  requires C, 67.5; H, 5.9%).

The carbinol can also be prepared by dissolving the quinonoid or the lactone form in aqueous sodium carbonate or hydroxide and, after the dark red colour has disappeared, acidifying the solution with hydrochloric acid. An alkaline solution of the carbinol quickly decomposes in contact with air; from the products of decomposition phenol and *p*-hydroxybenzoic acid have been isolated.

*Phenol- $\beta$ -methylglutarein.*—Only the lactone form of this compound was obtained by the method for preparing phenolglutarein. The carbinol derivative was obtained by keeping a solution of the lactone in dilute aqueous sodium hydroxide until the pink colour had disappeared, and then acidifying with dilute hydrochloric acid, filtering off the precipitated lactone, and extracting the filtrate with ether; on rapidly evaporating the ether in a current of air, the carbinol was obtained as a colourless, crystalline substance which in the course of about 15 minutes changed completely into the lactone. Immediately after isolation, it dissolves in aqueous sodium hydroxide, forming a colourless solution, but in a few minutes this begins to exhibit the red colour of the quinonoid form. Under no conditions could the carbinol be obtained in a stable form.

*Phenol- $\beta\beta$ -dimethylglutarein.*—A mixture of 16 g. of  $\beta\beta$ -dimethylglutaric acid, 25 g. of phenol, and 13 c.c. of stannic chloride was heated on the steam-bath for about 4 hours; after cooling, the dark red melt was dissolved in moist ether. The ethereal solution was thoroughly washed with ice-cold dilute hydrochloric acid, water, and sodium bicarbonate solution, and then shaken with a saturated solution of sodium carbonate for 3 hours. The aqueous layer was separated, acidified with hydrochloric acid, and distilled in steam



to remove phenol. The yellow, sticky residue was extracted with ether, the ether evaporated, and the residue thus obtained was acetylated by boiling with twice its volume of acetic anhydride and a few drops of pyridine. The excess of anhydride was decomposed with water, and the viscous acetyl derivative dissolved in ether. The ethereal solution was repeatedly extracted with a 5% solution of sodium hydroxide until the extract was no longer pink. The ether was then evaporated, and the residual acetyl derivative hydrolysed by dissolving it in concentrated sulphuric acid and pouring the solution on to ice. The lactone was precipitated in pinkish-white flocks, which were filtered off, washed with water, dissolved in ether, the ethereal solution shaken with sodium bicarbonate solution, decolorised with animal charcoal, dried, and then allowed to evaporate at the ordinary temperature. Large, white, cubical crystals were obtained which were freed from the adhering sticky matter by washing with absolute alcohol-ligroin and then recrystallised from ether or dilute alcohol; large, transparent, silky prisms were thus obtained (yield about 1.3 g.).

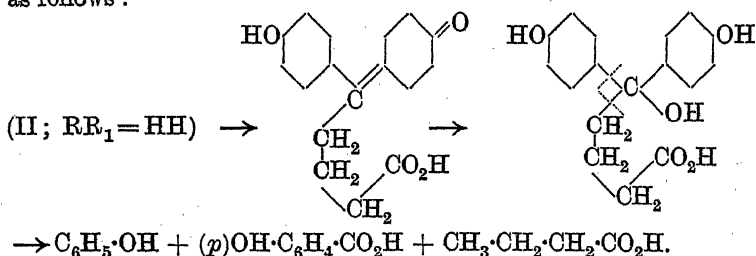
Phenolglutareins were obtained from  $\beta\beta$ -methyleneethyl-,  $\beta\beta$ -diethyl-, and  $\beta$ -cyclohexane-glutaric acids in similar ways to the above.

*Decomposition of Phenolglutarein by Alkali.*—Phenolglutarein (5 g.) was dissolved in 200 c.c. of 10% sodium hydroxide solution, and the mixture heated under reflux for about 3 hours. The solution was diluted with water, acidified with hydrochloric acid, and distilled in steam until phenol ceased to pass over. The residual liquid, after cooling, was extracted with ether, and from the ethereal extract 0.7 g. of *p*-hydroxybenzoic acid, m. p. 213°, was obtained.

The steam distillate, which had an acid reaction, was neutralised with sodium carbonate and extracted with ether. After the evaporation of the ether, a small quantity of a liquid smelling strongly of phenol was obtained which gave all the reactions of this substance. The aqueous mother-liquor, on evaporation to dryness, yielded about 1 g. of a solid which was qualitatively shown to be a mixture of sodium butyrate with smaller quantities of sodium acetate and succinate.

Phenolsuccinein, on treatment with sodium hydroxide, behaved in an exactly similar manner. Substituted phenol-succineins and -glutareins do not yield *p*-hydroxybenzoic acid on treatment with alkali but decompose into phenol and aliphatic acids in the manner described in J., 1924, 125, 2529, for the corresponding resorcinol derivatives.

The decomposition of phenolglutarein by alkali may be represented as follows :



The succineins and glutareins are fairly easily soluble in alcohol, acetone, acetic acid, or benzene and insoluble in water or ligroin.  $\alpha$  is the absorption maximum (wave-lengths) for dilute aqueous solutions.

#### *Phenolsuccineins.*

	Appearance.	M. p.	Colour in alkali.	$\alpha$ (2 mols. KOH).	$\alpha$ (20 mols. KOH).	Analysis (calc. % in brackets).
Phenol-	Colourless prisms.	252°	Deep bluish-pink.	5350	5450	C, 71.3 (71.1); H, 5.5 (5.2).
Phenoldimethyl-	"	225	Light pink.	5220	5280	C, 72.2 (72.5); H, 6.3 (6.0).
Phenolmethyl-ethyl-	Colourless silky needles.	192	"	5210	5280	C, 73.4 (73.1); H, 6.5 (6.4).
Phenoldiethyl-	"	260	"	5170	5200	C, 73.3 (73.6); H, 6.9 (6.7).
Phenolcyclohexane-	Colourless glistening leaflets.	257	"	5070	5100	C, 74.1 (74.3); H, 6.9 (6.8).

#### *Phenolglutareins.*

Phenol-	Colourless needles.	145—147	Deep bluish-pink.	5510	5540	C, 71.5 (71.8); H, 5.9 (5.6).
Phenolmethyl-	"	249	"	5470	5490	C, 72.2 (72.5); H, 6.3 (6.0).
Phenoldimethyl-	"	185	Reddish-pink.	5420	5450	C, 72.8 (73.1); H, 6.7 (6.4).
Phenolmethyl-ethyl-	"	164—165	"	5420	5450	C, 73.5 (73.6); H, 6.6 (6.7).
Phenoldiethyl-	"	181	"	5380	5410	C, 74.4 (74.1); H, 7.3 (7.0).
Phenolcyclohexane-	"	135	"	5210	5310	C, 74.6 (74.8); H, 7.3 (7.1).

*Rate of Transformation of the Lactonoid Phenolglutareins into the corresponding Carbinol Derivatives by the Action of Alkali.*—1 C.c. of an *N*/100-alcoholic solution of the phenolglutarein was added to 10 c.c. of aqueous potassium hydroxide of definite strength, and the time (seconds) required for the disappearance of the red colour thus produced was noted. The experiments were conducted at about 22° under even conditions of illumination. The results were as follows :

Glutarein.	Strength of potassium hydroxide solution.								
	2 <i>N</i> .	<i>N</i> .	<i>N</i> /2.	<i>N</i> /10.	<i>N</i> /50.	<i>N</i> /100.	<i>N</i> /200.	<i>N</i> /500.	<i>N</i> /1000.
Phenol-	485	423	422	422	422	422	422	Long time!	Very long time.
Phenol-methyl-	465	412	409	409	409	405	405	„	„
Phenoldi-methyl-	440	405	405	405	405	405	405	„	„
Phenol-methyl-ethyl-	430	405	401	400	400	400	400	„	„
Phenol-diethyl-	235	168	132	188	105	105	134	192	Long time
Phenolcyclo-hexane-	70	67	57	49	39	48	59	235	„

My best thanks are due to Professor J. F. Thorpe for the kind interest he has taken in this work and to the Chemical Society for a grant which has defrayed a part of the expense.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

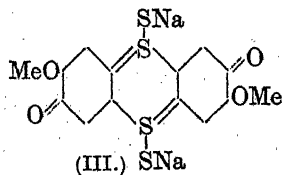
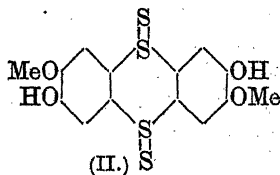
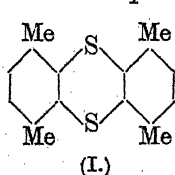
SOUTH KENSINGTON.

[Received, October 30th, 1925.]

## CXLVIII.—*Synthesis in the Thianthren Series.* *Part II.*

By MONMOHAN SEN and JÑANENDRA NATH RÂY.

THE method described in Part I (J., 1921, 119, 1959) has been applied in the synthesis of other thianthren derivatives. The reaction is apparently a general one, but difficulties are encountered in purifying the product. *Tetramethylthianthren* (I) has been obtained in the crystalline form and characterised by the preparation of its *disulphone*.



From guaiacol, *dimethoxydihydroxythianthren disulphide* (II) was obtained, the crystalline yellow sodium salt of which is sparingly soluble in water. The similar disulphide previously isolated (*loc. cit.*) was very unstable. The remarkable stability of the present compound may possibly be due to its acquiring a *p*-quinonoid constitution (III); the sodium salt forms an orange solution in water.

In view of the use of thioaniline in the dye industry, it appeared that diaminothianthren might be a valuable intermediate, and some azo-compounds derived from this base have been prepared.

#### EXPERIMENTAL.

**1:4:5:8-Tetramethylthianthren (I).**—When dry aluminium-mercury couple (from 0.3 g. of aluminium foil) was added to a mixture of *p*-xylene (6 c.c.) and sulphur monochloride (4 c.c.), the reaction became vigorous in a few minutes and hydrogen chloride was copiously evolved. The mass soon solidified almost completely and carbon disulphide (8 c.c.) was then introduced and the mixture kept at 40° during an hour. The solvent was decanted, the product decomposed with ice, and the colourless precipitate washed successively with yellow ammonium sulphide, aqueous sodium sulphite, and water, dried, and crystallised from boiling nitrobenzene. The crystals were extracted with boiling carbon disulphide, and dissolved in nitrobenzene, the last trace of sulphur being then removed by treatment with copper powder. The filtrate from the copper sulphide deposited the pure substance in colourless needles, m. p. 242° (Found: S, 23.1; C, 70.6; H, 5.8.  $C_{16}H_{16}S_2$  requires S, 23.5; C, 70.5; H, 5.8%).

The substance exhibits the normal behaviour of thianthren and dissolves in concentrated sulphuric acid to a green solution which is decolorised on dilution with water, the original compound being precipitated.

The *disulphone* was obtained by repeatedly evaporating the thianthren with an excess of nitric acid (*d* 1.4) on the steam-bath. The product was precipitated with water, washed, and crystallised from glacial acetic acid, separating in needles, which did not melt below 290° (Found: S, 18.7.  $C_{16}H_{16}O_4S_2$  requires S, 19.0%).

**3:7-Dimethoxy-2:6-dihydroxythianthren Disulphide.**—To a solution of 6.2 g. of guaiacol in 10 c.c. of carbon disulphide, 4 c.c. of sulphur monochloride, dissolved in 10 c.c. of the same solvent, were added and the amalgam prepared from 0.4 g. of aluminium was quickly introduced. The solution became deep green and a vigorous reaction ensued. After being kept at room temperature

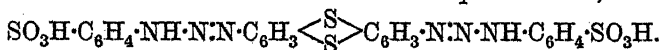
for an hour, the mixture was warmed at 40° for some time, the carbon disulphide evaporated off, and the residue treated with water. The red oil thus obtained was dissolved in alkali. The filtered solution slowly deposited glistening, yellow leaflets. These were filtered off, dissolved in water, and the thianthren derivative precipitated by carbon dioxide. The yellow solid thus obtained crystallised from boiling alcohol in yellow, silky scales, m. p. 202° (Found: S, 33.9.  $C_{14}H_{12}O_4S_4$  requires S, 34.4%). The yield was poor.

The substance was easily acetylated by boiling with an excess of acetic anhydride and a few drops of pyridine. The *diacetyl* derivative crystallised from alcohol in needles, m. p. 165° (Found: S, 27.7; C, 47.5; H, 3.6.  $C_{18}H_{16}O_6S_4$  requires S, 28.0; C, 47.3; H, 3.5%).

*Azo-compound from Diazotised Diaminothianthren and  $\beta$ -Naphthol.*—A solution of 2 g. of diaminothianthren (*loc. cit.*, p. 1964) in 200 c.c. of water and 1 c.c. of concentrated hydrochloric acid was treated at 0° with 0.44 g. of sodium nitrite and thereafter with an alkaline solution of 0.9 g. of  $\beta$ -naphthol. The solid precipitated on acidification was crystallised from boiling benzene (Found: N, 10.6.  $C_{32}H_{20}O_2N_4S_2$  requires N, 10.1%). The deep red dye produced a dull shade on unmordanted cotton.

*Tetrazo-compound from Diaminothianthren and Resorcinol.*—Diaminothianthren hydrochloride (2 g.) was diazotised and then coupled with 0.17 g. of resorcinol in alkaline solution. The dye obtained on acidification could not be crystallised, and therefore it was purified by precipitation from an alkaline solution. The reddish-brown product did not melt below 250° (Found: N, 11.4.  $C_{24}H_{16}O_4N_4S_2$  requires N, 11.5%).

*Thianthren-2 : 6-bis(diazoaminobenzene-4'-sulphonic Acid,*



—A solution of 1.1 g. of sulphanilic acid in water containing sodium hydroxide was diluted to 200 c.c., made faintly acid, and slowly treated with a diazotised solution of 2 g. of diaminothianthren. The mixture was filtered after a time, and the filtrate made alkaline and then acidified with acetic acid. The reddish-brown dye thus precipitated was dried (Found: N, 12.8.  $C_{24}H_{18}O_6N_8S_4$  requires N, 13.6%).

Thianthren derivatives were obtained by the general method in the following cases, but the products could not be isolated free from sulphur: bromobenzene, *p*-chlorophenol, *p*-cresol, quinol dimethyl ether, *p*-tolyl methyl ether, and resorcinol dimethyl ether. The case of bromobenzene is interesting, because, unlike that in

iodobenzene (*loc. cit.*), the halogen atom is not displaced in the reaction.

We wish to thank Dr. A. F. Titley of Oxford for a gift of pure *p*-xylene.

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### CXLIX.—*The Hydrates of Chromic Nitrate.*

By JAMES RIDDICK PARTINGTON and SIDNEY KEENLYSIDE  
TWEEDY.

IN the course of investigations on chromium salts, it was necessary to prepare crystals of chromium nitrate. Chromic hydroxide, precipitated from cold, saturated chrome alum solution, and washed with hot water, was dissolved in the least possible quantity of cold nitric acid (about 4*N*; compare Loewel, *J. Pharm. Chim.*, 1845, 7, 321, 401). The dark green dichroic solution thus obtained was allowed to crystallise in an open dish; after a few days it turned violet, and was then transferred to a stoppered bottle. Some three months later, it had deposited reddish-violet crystals and reverted to its original green colour. The crystals were not deliquescent and appeared through the microscope to be octahedral. After drying between filter-paper, they gave Cr, 11.2, 11.15; N, 9.0, 9.0% (determined by reduction with Devarda's alloy; very low results are obtained if the reaction is not allowed to finish in the cold after the initial warming necessary to start it) [ $\text{Cr}(\text{NO}_3)_3 \cdot 12\frac{1}{2}\text{H}_2\text{O}$  requires Cr, 11.2; N, 9.1%]. Large crystals were also grown.

The "normal" chromic nitrate described in text-books (*e.g.*, Roscoe and Schorlemmer, 1923, vol. ii, p. 1084) forms deliquescent rhombohedra,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . By allowing a solution of chromic hydroxide in dilute nitric acid to evaporate spontaneously, Halse (*Chem.-Ztg.*, 1912, 36, 962) obtained from a violet solution crystals of a hydrate,  $\text{Cr}(\text{NO}_3)_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ , m. p. about 100°, which he considered to be identical with a brown, crystalline hydrate obtained by Jovitschitsch (*Monatsh.*, 1912, 33, 9), who heated ignited chromic anhydride with nitric acid (*d* 1.4) in a sealed tube for 1½ hours at 160°. It seems, however, that the crystals obtained by Halse are identical with those obtained by us and contain  $12\frac{1}{2}\text{H}_2\text{O}$ . Our crystals turned black (viewed by reflected light) at 95° and melted to a dark green liquid at 104–105°. Halse remarks that these crystals, since they are formed by the action of an acid on a hydr-

oxide, should be considered as the "normal" form of chromium nitrate in preference to the nonahydrate, which is only obtained under special conditions.

On one occasion, in a repetition of Halse's experiment, the liquid evaporated to a dark green syrup which retained its colour both on boiling and on dilution. Attempts were made to precipitate the green form of chromic nitrate from the syrup. Anhydrous ether and ether mixed with nitric acid were ineffectual, but addition of excess of absolute alcohol threw out a light green precipitate which, after drying between filter-paper, had a m. p. about 74°. No precipitation occurred on the addition of 96% alcohol. A quantity of the substance is being prepared with a view to future investigation.

We repeated Jovitschitsch's preparation with pure chromic anhydride prepared by the action of sulphuric acid on potassium dichromate (Traube, *Annalen*, 1848, 66, 165) and purified by grinding with concentrated nitric acid, draining and heating at 80° in a current of dry air. The bomb tubes used in the preparation of the nitrate are very liable to burst during the heating. On only one occasion a brown solution was obtained which deposited brown crystals on keeping in a vacuum desiccator over potassium hydroxide. On all other occasions, the ordinary blue-violet dichroic solution of chromic nitrate was obtained, which yielded crystals of the nonahydrate. The factors controlling the production of the brown solution were not discovered. The brown crystals gave a brownish-green dichroic aqueous solution; the filtrate obtained after precipitating with ammonia was pale yellow, indicating that a small portion of the chromium is present in the crystals as chromate [Found: Cr, 13.3. Calc. for  $\text{Cr}(\text{NO}_3)_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ : Cr, 13.9%]. No crystals were available for checking this figure, or for determining the nitrogen.

Jovitschitsch remarks that the brown crystals on drying over potassium hydroxide and even over calcium chloride lose both nitric acid and water; later, he says that, after 5 days over calcium chloride,  $\text{Cr}(\text{NO}_3)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$  is formed. We kept 0.2522 g. of the crystals over sodium hydroxide; after 4 days they turned a dull violet and weighed 0.2222 g., this weight remaining constant for 12 days [Found: Cr, 15.1; N, 12.35. Calc. for  $\text{Cr}(\text{NO}_3)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ : Cr, 16.3; N, 13.1%].\* None of these figures is to be regarded as final.

The viscosities,  $\eta$ , of solutions of the nonahydrate of chromium nitrate (Kahlbaum's pure; see below) were determined by the

\* Dr. A. D. Mitchell has pointed out to us that the values found are very nearly those required for  $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

comparative flow method at 18° and 25°. The modified Ostwald viscosimeter described by Martin was used (*Bull. Soc. chim. Belg.*, 1925, 34, 81); we have found this instrument to give very consistent results. The viscosimeter was standardised with freshly-prepared conductivity water obtained from a Bousfield still and stored in a Pyrex flask; water similarly prepared was used for making the solutions. Each viscosity ratio represents at least a dozen consecutive identical time readings or else the mean of a dozen or more readings the extreme variation of which is 0.5 second. The time of flow for water was 31.5 seconds at 25° and 36.5 seconds at 18°.  $w$  is the weight of anhydrous salt in 100 g. of water.

Temperature 18°.			Temperature 25°.		
$w$ .	$\eta/\eta_{H_2O}$ .	$\eta$ .	$w$ .	$\eta/\eta_{H_2O}$ .	$\eta$ .
29.11	1.8219	0.01948	25.37	1.6428	0.01498
26.58	1.7055	0.01823	18.58	1.4048	0.01281
23.62	1.5616	0.01669	12.61	1.2302	0.01122
19.73	1.4247	0.01523	10.98	1.1984	0.01093
15.07	1.2841	0.01373	8.99	1.1508	0.01050
9.56	1.1422	0.01221	6.05	1.1032	0.01006
7.16	1.0960	0.01172	5.93	1.0952	0.00999
4.99	1.0582	0.01131	3.58	1.0556	0.00963
3.55	1.0308	0.01102	3.18	1.0476	0.00953
			1.91	1.0238	0.00934

Measurements at higher dilutions are unsatisfactory with the method used.

The figures given in the third and sixth columns represent the absolute viscosities, obtained by multiplying  $\eta/\eta_{H_2O}$  by  $\eta_{H_2O}$ . Thorpe and Rodger (*Phil. Trans.*, 1894, 185, 397) give 0.00891 and 0.010563 dyne/cm.<sup>2</sup> at 25° and 18°, respectively, for  $\eta_{H_2O}$ ; we have used the more recent values determined by Leroux (*Ann. Physique*, 1925, 4, 163), namely, 0.00912 and 0.01069 dyne/cm.<sup>2</sup>, the former figure being calculated on the assumption that the viscosity varies linearly with the temperature over the range 23.2° to 26.4°, for which  $\eta = 0.00949$  and 0.00883 dyne/cm.<sup>2</sup>, respectively. The above values for the viscosities of chromium nitrate solutions lie on smooth curves.

Kahlbaum's pure chromic nitrate crystals,  $Cr(NO_3)_3 \cdot 9H_2O$  (Found: Cr, 13.0; N, 10.7. Calc.: Cr, 13.0; N, 10.5%), freed from adhering nitric acid by pressing between filter-paper, melted to a dark green liquid at 66–66.5°; there were no signs of fusion at the previously recorded m. p., 36.7° (Ordway, *Amer. J. Sci.*, 1850, 9, 30). The fused salt on cooling passed through an indefinite pasty stage extending from about 37° to 20°, and gradually changed in colour to a greyish-green. On continual stirring, the temperature rose to 30–33° and slow crystallisation set in. The crystals were violet. These temperatures are slightly different from



those recorded by Ordway, who found that the green liquid first deposited crystals at  $24^{\circ}$ , the temperature rising gradually to  $34^{\circ}$ . A crystal picked out of the green paste melted sharply at  $66.5^{\circ}$  and was evidently, therefore, a crystal of nonahydrate. Apparently no transition to a second hydrate takes place at the m. p.

Chromic nitrate nonahydrate crystals may be readily prepared by dissolving violet chromic chloride in slightly more than the theoretical quantity of hot strong nitric acid and storing in a vacuum desiccator over sodium hydroxide. If excess of the chloride is used, the product contains small quantities (0.1%) of chlorine. No chromic chloride nitrate similar to that prepared by Schiff by dissolving basic chromic chloride in nitric acid (*Annalen*, 1862, 124, 177) was obtained.

An X-ray examination of chromium nitrate and other chromium salts is being undertaken. It is expected that information of importance for the theory of co-ordination will be obtained with the three isomeric hexahydrates of chromic chloride, all of which have been prepared.

#### *Summary.*

1. The solution obtained by dissolving chromic hydroxide in nitric acid yields crystals of  $\text{Cr}(\text{NO}_3)_3 \cdot 12\frac{1}{2}\text{H}_2\text{O}$ , m. p.  $104-105^{\circ}$ , and not  $\text{Cr}(\text{NO}_3)_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ , as previously described.

2. The viscosities of some chromic nitrate solutions at  $18^{\circ}$  and  $25^{\circ}$  are recorded.

3. Chromic nitrate nonahydrate crystals melt at  $66-66.5^{\circ}$ , no transition to a second hydrate occurring at this temperature.

4. Chromic nitrate nonahydrate crystals may be prepared by dissolving violet chromic chloride in hot nitric acid and allowing the solution to crystallise in a vacuum desiccator.

In conclusion, one of the authors (S. K. T.) wishes to express his gratitude to the Advisory Council of the Department of Scientific and Industrial Research for a personal grant.

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*Hæmoglobin.*

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON  
FEBRUARY 11TH, 1926.

By JOSEPH BARCROFT, C.B.E., M.A., F.R.S.

IN making some remarks to-night about one of the subjects dearest to my heart, namely, hæmoglobin, I wish to disabuse you at the outset from any idea that my primary object is to inform you—far otherwise—hæmoglobin is to me a query mark—an unanswered question—a Will-o'-the-wisp—something which one day you think you have grasped only to find the next that its real essence has eluded you. You recollect what Thackeray said about George IV : “To make a portrait of him at first seemed a matter of small difficulty. There is his coat, his star, his wig, his countenance simpering under it : with a slate and a piece of chalk I could at this very desk perform a recognisable likeness of him. And yet after reading of him in scores of volumes, and hunting him through old magazines and newspapers, having him here at a ball, there at a public dinner, there at races and so forth, you find you have nothing—nothing but a coat and wig and a mask smiling below it—nothing but a great simulacrum. . . . I look through all his life and find but a bow and a grin—I try and take him to pieces, and find silk stockings, padding stays, a coat with frogs and a fur collar, a star and a ribbon, a pocket handkerchief prodigiously scented, one of Truefitt's best nutty-brown wigs reeking with oil, a set of teeth and a huge black smock under-waistcoat, more under-waistcoats and under that nothing.” And so in my more despondent moments it seems to be with hæmoglobin. Its colour fascinates you, you crystallise it only to find that it crystallises in innumerable forms, you determine its osmotic pressure to find that may be anything, you redissolve the crystals to find that the material has altered as the result of crystallisation. Is the attempt to pursue hæmoglobin worth while? Well, gentlemen, at the end of this lecture you may answer that question as you will. For my part it is just here that the analogy with “The first gentleman in Europe” breaks down, for you must remember that Thackeray went on : “I own I once used to think it would be good sport to pursue him, fasten on him, pull him down. But now I am ashamed to mount and lay good dogs on to summon a full field and then to hunt the poor game.” Hæmoglobin never can appear poor game to the biologist, for the life of the warm-blooded animal—yours and mine—depends upon its existence, there is no other substance which is capable of transporting oxygen

in just the same amount and in just the same way. How nature discovered the pieces from which to effect the synthesis must ever be a fascinating subject of inquiry to the biologist—and to find out what those pieces are and in what way the synthesis has been effected he must digress from his own proper sphere into that of chemistry. Yet as ribbons, wigs, and stars go, those of George IV were probably more interesting than most, and if I at once disclaim the objects of telling what hæmoglobin really is, and make it clear that I am merely trying to pass an hour by discussing some of its more superficial properties, it may be that you will find these a little interesting, even if you regard the methods of the biologist as being at one time crude and at another clumsy, and his presentation of a chemical problem naïve and amateurish.

### I.

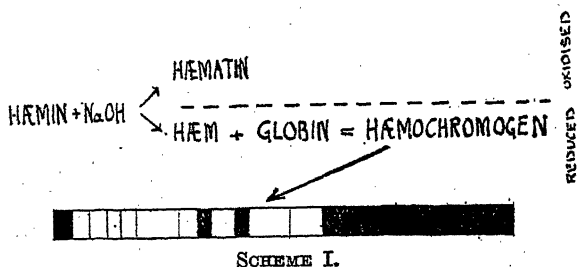
The time-honoured conception of hæmoglobin was that it consisted of two moieties united in some unknown way. These were called hæmatin and globin, the latter being a protein, the former a substance containing iron. It was supposed further that these could be broken the one from the other by acid or alkali. Within the last two years the position as put forward above has been gone into in considerably greater detail. Let us start with hæmoglobin and work backwards. If in the presence of a reducing agent hæmoglobin be made alkaline, a substance, hæmochromogen, is formed with a characteristic spectrum, which possesses a band of great density in the region of  $\lambda 560$ . This substance was assumed to be hæmatin, in the reduced form and in alkaline solution. That is to say, it was assumed to be protein-free. This conception appears to be incorrect, for we can obtain hæmochromogen, not analytically, but synthetically, the best starting point being a substance called hæmin.

Hæmin is made by adding glacial acetic acid to dried blood in the presence of sodium chloride and is a well-defined crystalline substance to which the formula  $C_{34}H_{35}O_3(?)N_4Fe.HCl$  was given by Hoppe-Seyler. From it, *in the presence of a reducing agent*, the base hæm,  $C_{34}H_{35}O_3N_4Fe(?)$ , may be liberated by the addition of sodium hydroxide. According to the old conception, this base should have been hæmochromogen, but it is not so, having a quite different and ill-defined spectrum. One further step is necessary to produce hæmochromogen, namely, the addition of globin to the hæm. Therefore we obtain the following scheme (Scheme 1).

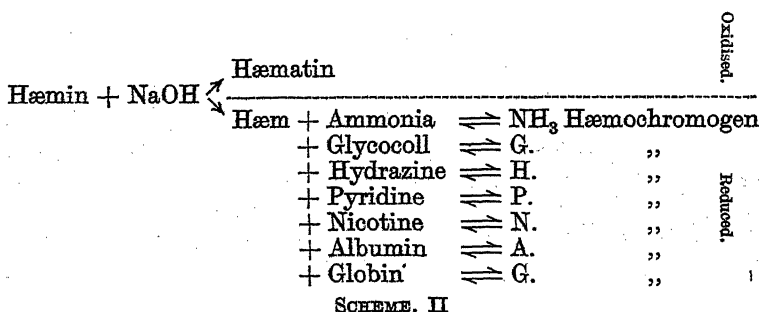
The conception put forward above opened up an entirely new field for discovery, in which three principal facts may be emphasised.

First, that globin is only one of a great many substances which

will perform the same function, thus forming a whole group of hæmochromogens. Nicotine, pyridine, hydrazine, ammonia,



albumin, etc., all perform the same rôle, that is, when added to hæm, which has a comparatively indistinct spectrum, they yield substances producing spectra with the typical characteristics of that of hæmochromogen, and it must be remembered that the spectrum of hæmochromogen is the most typical and best defined of all blood spectra. We therefore may now extend our scheme as follows :



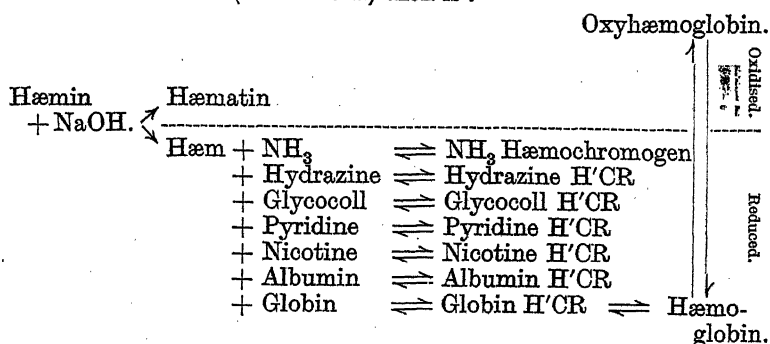
Secondly, whilst all these substances yield hæmochromogens with spectra of the same type, there are appreciable differences between the actual spectra of the different members of the family; in one the bands will be a little towards the red, in another a little towards the blue—but so little that casual observation would not show the difference.

Thirdly, all these hæmochromogens seem to be kept *in statu quo* as the result of balanced action, and here it may be noted that for the production of most of them a great preponderance of the components is necessary. The globin hæmochromogen stands nearly but not quite alone in so far as the action is almost complete.

The globin compound has as well other distinctive properties; it is one of the few hæmochromogens which are soluble in a high degree, and, but chiefly, the globin compound stands alone, in

that it and it only can form a hæmoglobin. Anson and Mirsky, by regulation of the hydrogen-ion concentration, obtained hæmoglobin from globin hæmochromogen. Robin Hill has been at great pains to obtain the analogues from other hæmochromogens, but without success.

The final scheme (Scheme III) then is :



SCHEME III.

## II. Cytochrome.

It is not possible to leave the subject of hæmochromogen without making a digression for the purpose of discussing cytochrome. Here, as in the case of hæmochromogen, let the name cytochrome stand for a spectrum, at all events until we can get something more concrete to which we may attach it.

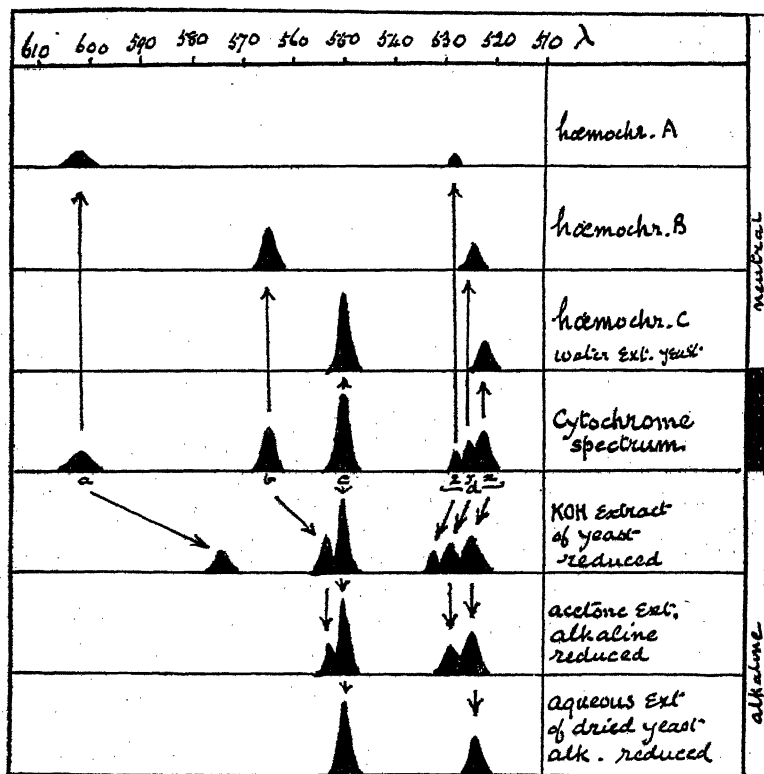
This spectrum was first described by McMunn,<sup>1</sup> but its true significance has only recently been brought to light by the work of Keilin,<sup>2</sup> who has kindly consented to demonstrate it to-night. It may be seen well in the wing-muscle of the bee, in the onion, in yeast, in aerobic bacteria, and, indeed, it may be regarded as of more or less universal occurrence in forms of life which have contracted the oxygen habit. In these there is reason to suppose that it acts as a catalyst, in contrast to hæmoglobin, which acts as a carrier, but pervading both the animal and the vegetable kingdom; it is far more widely distributed than either hæmoglobin or chlorophyll. Not only so, but cytochrome appears in forms of life than which none are more primitive.

This spectrum has never been seen outside a cell; all attempts to extract the cytochrome have ended in changing the spectrum—moreover, it is only seen in the reduced condition—shake yeast with air, the spectrum disappears, to return on permitting the yeast to reduce itself—expose the wing-muscle of the bee to the atmosphere, the spectrum disappears, to return on the exclusion of oxygen by a coverslip.

Superficially this spectrum presents the appearance of possessing four bands, which may be designated as *a*, *b*, *c*, and *d*; of these *c* is the most conspicuous (see Fig. 1).

To say that this spectrum has four bands is only a partial statement of the facts, for the band *d* may be resolved into three overlapping bands which I will call *x*, *y*, and *z*. Thus on any picture

FIG. 1.\*



which shows the relative absorption at different parts of the spectrum there are six summits. This is shown crudely in the figure. It must not be supposed that this figure is drawn from accurate spectrophotometric observations; the positions of maximum density only have been measured with care. So far as the relative densities of the various bands are concerned, the figure simply is a rough

\* Figs. 4, 7, 8, 9, 10, 11, 12, and 13 are reproduced by permission from the *Proceedings* of the Royal Society, and Figs. 5 and 6 from the *Journal of Physiology*.

representation of the impression one gets from the observation of varying concentrations of the material.

To obtain a better understanding of the cytochrome spectrum, let us turn to alkaline extracts. An extract of yeast in potassium hydroxide gives a spectrum also with six summits, but which has only three bands, because those which correspond to  $b$  and  $c$  have become merged into a single band with two summits. The summits in the spectrum of the potassium hydroxide extract I will call  $a_K$ ,  $b_K$ ,  $c_K$ ,  $z_K$ ,  $y_K$ , and  $x_K$ , respectively, representing  $a$ ,  $b$ ,  $c$ ,  $z$ ,  $y$ , and  $x$ .

If one goes further and makes an acetone extract, which is then made alkaline, only four summits appear; they are  $b_K$ ,  $c_K$ ,  $y_K$ , and  $z_K$ , respectively,  $a_K$  and  $x_K$  being absent. If one goes still further and dries the yeast, makes an aqueous extract of the dry yeast, and renders that alkaline, two more bands,  $b_K$  and  $y_K$ , drop out and one is left with  $c_K$  and  $z_K$  only. And now we have something very familiar; it is none other than a typical hæmochromogen spectrum. The simplest interpretation of the cytochrome spectrum is that it is a mixture of the spectra of three hæmochromogens A, B, and C, of which A is responsible for bands  $a$  and  $z$ , B for bands  $b$  and  $y$ , and C for bands  $c$  and  $x$ , and this interpretation is rendered the more likely by the fact that in different cytochromes the relative intensities of the bands vary. But in this respect the bands are associated in pairs; thus  $a$  and  $z$  may be exaggerated, relatively to the rest, or  $b$  and  $y$  may be, but not  $a$  and  $y$  or say  $c$  and  $z$ , or  $a$  or  $b$  or  $c$  alone.

### III. *Metallic Porphyrin Compounds.*

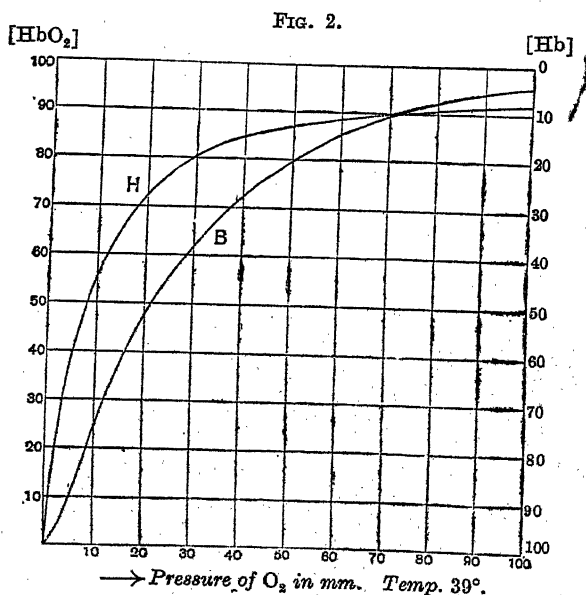
Some allusion should here be made to the work of Robin Hill,<sup>4</sup> who has investigated the compounds of various metals with porphyrin. Porphyrin unites with a great number of metals—iron, nickel, cobalt, manganese, zinc, copper, silver, potassium and others. The compounds formed are all on the *hæm* level, if I may put it that way, but of these, only three have the power of being readily oxidisable and reducible. These are the compounds of cobalt, iron, and manganese, *i.e.*, the hæmatins as well as the hæms of these metals can be obtained.

It is remarkable and perhaps significant that, whilst none of these substances has any nitrogenous compound attached, they all, with one exception, have spectra which suggest hæmochromogen rather than hæm. The one exception is the iron compound, and, further, it is the only one to which nitrogenous compounds such as pyridine and globin will attach themselves and thus form true hæmochromogens. Not that the iron-porphyrin compound is precisely the same as hæm, or that the derived hæmochromogens are precisely the same as those formed from blood—the spectral bands are nearer the blue;

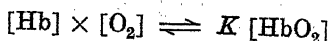
presumably the original porphyrins are not the same as that in the hæm obtained from blood.

#### IV. *Equilibrium Constants of Compounds of Hæmoglobin with Oxygen and Carbon Monoxide.*

The curve which represents the equilibrium between oxygen and blood is, as was shown by Christian Bohr,<sup>5</sup> S-shaped in character (Fig. 2, B). This contour adds greatly to the biological value of hæmoglobin and for that reason it was an object of speculation to Bohr himself—as it has been to all his successors—as to what



the underlying significance of the inflexion might be. A simple equilibrium of the type



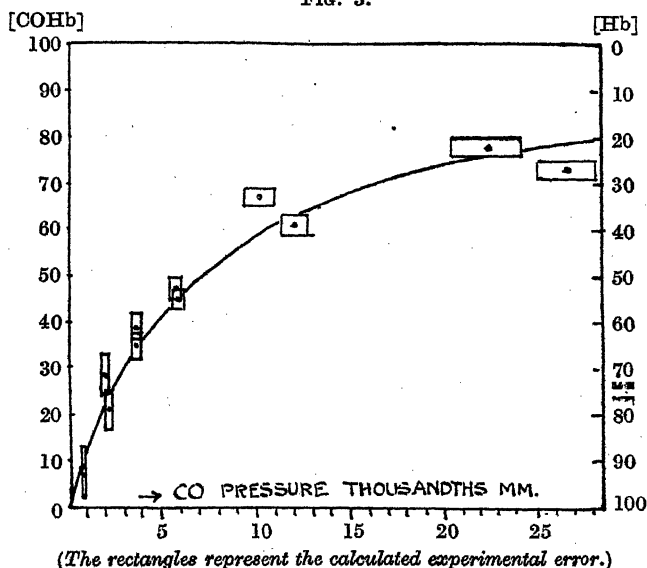
would, of course, be represented by a rectangular hyperbola.

In 1911, Roberts and I<sup>6</sup> found that a dialysed solution of hæmoglobin of considerable purity yielded an equilibrium curve which approximated very much to the hyperbolic type, and we hazarded the view that if complete purity were obtained the curve would actually become a hyperbola (Fig. 2, H). This view met with a general, but as it seems a premature, acceptance; for, on later occasions with I think purer and certainly more concentrated



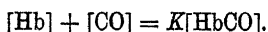
solutions, we failed to obtain the hyperbolic form, and at Harvard, Adolph and Ferry,<sup>7</sup> with a very perfect technique of its kind, asserted that in no circumstances was the curve anything but S-shaped. I used the phrase "a very perfect technique"—perhaps this phrase was wrong. I should have said a technique which more nearly reached our ideals. Our ideals were: a solution which contained the minimum of impurity and the maximum of hæmoglobin. With regard to the latter point, of course the greater the concentration of hæmoglobin the easier and more trustworthy becomes the gas analysis.

FIG. 3.



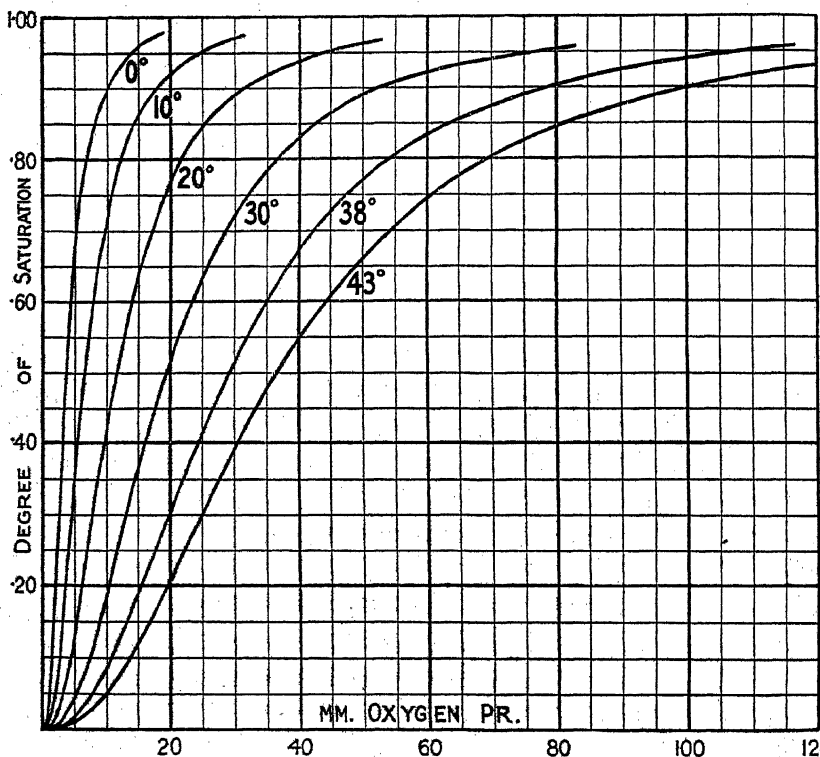
The conceptions put forward by Adair<sup>8</sup> indicated the probability of our ideal being wrong. They suggested that the fundamental equilibrium curve was to be obtained from the investigation of solutions not stronger but more dilute than that used by Roberts and myself. The study of such solutions required an entirely new technique. The relative concentrations of hæmoglobin and oxyhæmoglobin in dilute solution can be determined only by some spectroscopic method, and even that is very difficult to do and can be done only for the middle portion of the curve. The pressures of oxygen involved are so small as to demand very exact and difficult analyses of the atmosphere to which the hæmoglobin is exposed, if the equilibrium be struck at room temperature. On the other hand, if the equilibrium be struck at 35–40°, the gas analysis

becomes easy, but the hæmoglobin becomes unstable. If we review these difficulties in order, we find that the spectroscopic analysis becomes easy when we study the analogous reaction :



The difficulties of gas analysis by ordinary methods are, however, seemingly insuperable, for the pressures of carbon monoxide

FIG. 4.



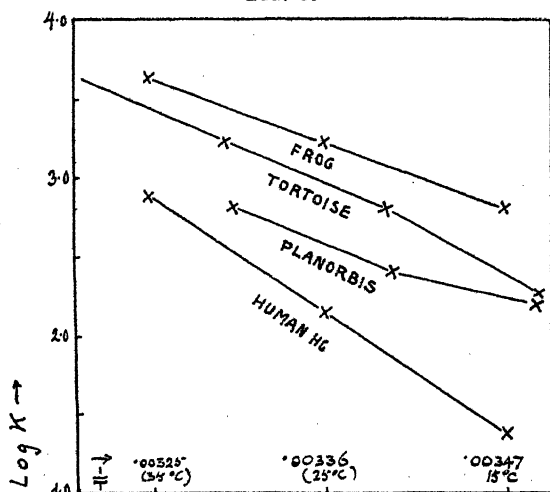
involved are counted in thousandths of a millimetre. Fortunately, it has proved possible at 15° to work out a method—almost audacious in its simplicity—which has enabled us to avoid gas analysis and by a single spectroscopic measurement to estimate the concentrations of all the reacting substances in the above equation. This technique will be demonstrated by my colleague, Dr. Selig Hecht, of Harvard. With its aid we have succeeded in the last fortnight or so in obtaining the curve shown in Fig. 3. Between the limits of 0 and 25

thousandths of a millimetre pressure of carbon monoxide (above which limits the method has not so far proved accurate) the curve is nearly, though not quite, hyperbolic in form.

It would seem that at last we are really within sight of the fundamental curve and in a position to push forward and discover the effects on this curve of increasing the concentration of hæmoglobin, of the salts, and of alterations in the concentration of hydrogen and hydroxyl ions in the solution.

I need only remind you that the effect of increasing alteration of hydrogen-ion concentration is to reduce the affinity of oxygen (or carbon monoxide) for hæmoglobin proportionately over the whole curve.

FIG. 5.

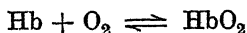


*The Temperature.*—The same may be said of the effect of temperature. The curves in Fig. 4 show the equilibrium of oxygen and hæmoglobin in blood at various temperatures. They are taken from a research by W. E. Brown and A. V. Hill.<sup>9</sup>

Their work has been followed by that of Maçela and Seliskar,<sup>10</sup> who have determined the temperature coefficients of the hæmoglobin, in dilute solution and under constant conditions of hydrogen-ion concentration, of several forms of life. It is remarkable, and again of great biological interest, that the hæmoglobin of man has a temperature coefficient of about 5 for its equilibrium with oxygen (Fig. 5), and that of the frog has a temperature coefficient of only about 2.5 (Fig. 6). Whether human hæmoglobin serves man better by having so high a temperature coefficient is difficult to say, but it would be quite unsuited to the needs of the frog.

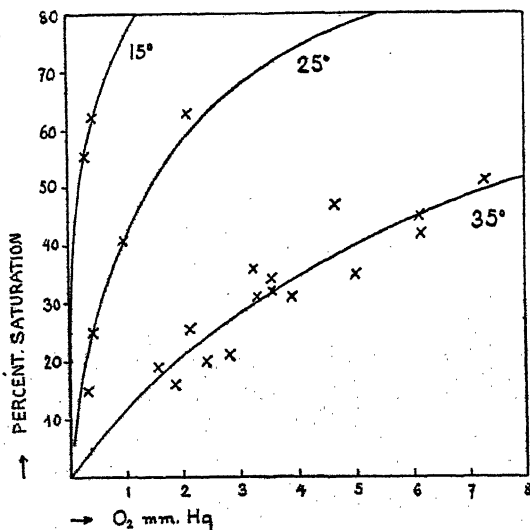
V. *The Velocity Coefficients of the Reactions of Hæmoglobin with Oxygen and Carbon Monoxide.*

The sensitiveness of the equilibrium constant of the reactions

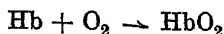


to temperature, hydrogen-ion concentration, etc., naturally leads to the inquiry how are the velocity coefficients of the separate phases of the reaction affected by the conditions under which the reaction takes place. If, for instance, a rise of temperature tends to

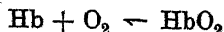
FIG. 6.



dissociate oxygen from hæmoglobin, is this because the velocity coefficient,  $k$ , of the reaction



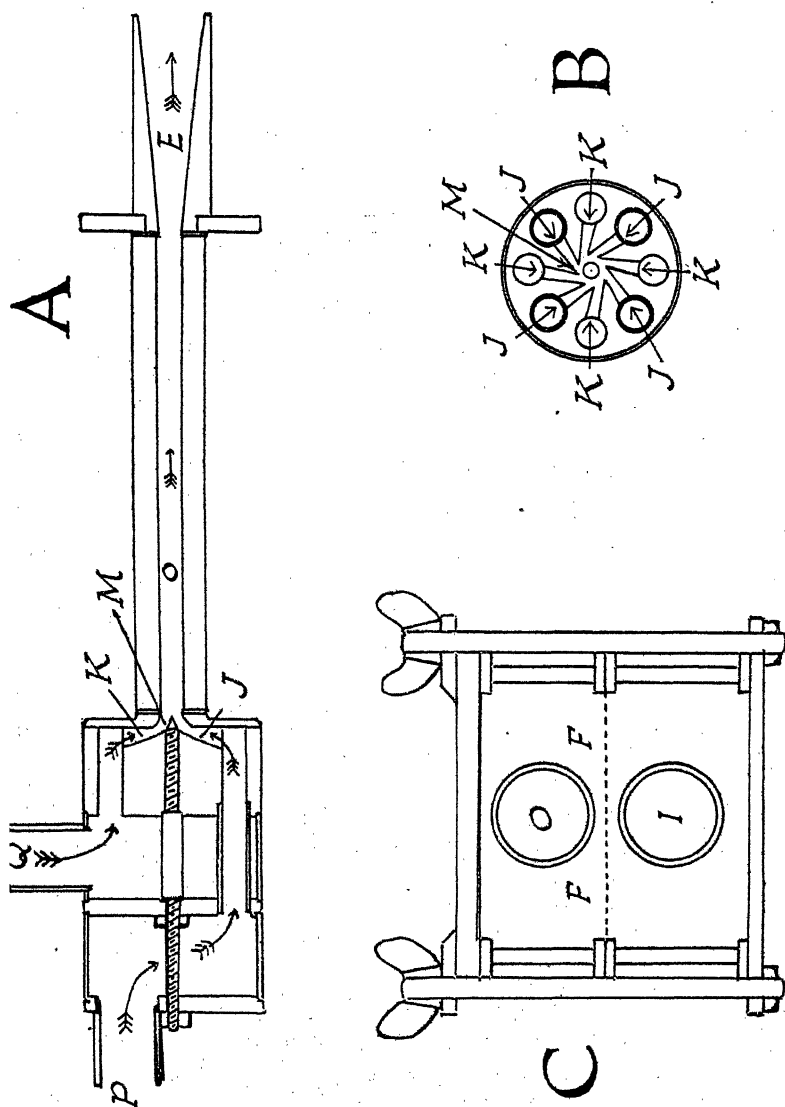
is increased or the velocity coefficient,  $k'$ , of the reaction



is diminished, or are both velocities increased but in different proportions—the state of affairs which would seem most probable *prima facie*—or what? Before the war, A. V. Hill and I made a few experiments on this subject, but it was clear that our experimental methods were quite inadequate—our scheme in general depended on the bubbling of oxygen or nitrogen through hæmoglobin solutions. The actual velocities of the chemical reactions which took place were of so high an order as compared with the rates at which the

gases passed into or out of the solution that the results which we obtained depended merely on the extent to which we were able to

FIG. 7.

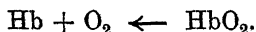


“ring the changes” on the physical, as opposed to the chemical, processes involved.

Within the last four years the velocity coefficients of the various

phases of the reactions of hæmoglobin with oxygen and with carbon monoxide have been studied by Hartridge and Roughton<sup>11</sup> with what appears to me to be amazing success. Such a study, of course, demands the most meticulous consideration of detail, and if I treat their method in a very general way it is because the discussion of the details, once embarked upon, would occupy more than the whole time at my disposal.

Let us commence, then, with the consideration of the reaction :

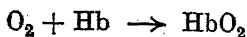


To carry out our purpose, it is necessary that one or other of the substances produced, the hæmoglobin or the oxygen, should be removed from the sphere of action as fast as it is formed. For this purpose, the procedure is briefly as follows.

The apparatus (Fig. 7) is schematically in the shape of a Y made of tubing—along the limbs of the Y enter on one side a dilute solution of the oxide of hæmoglobin, on the other water containing a concentration of sodium hyposulphite to absorb the oxygen, it being ascertained that the sodium hyposulphite does not reduce the oxide by double decomposition. At the junction of the tubes there is a mixing chamber, in which the mixing is so rapid and intimate as to be completed in a time which is negligible compared with the one-hundredth part of a second. The rate at which these fluids are driven through the apparatus is so great that the reaction in the lower limb of the Y may be followed with the eye. The fluid, which emerges red from the mixing chamber, is seen to become purple as it passes down the tube. The degree of reduction may be estimated at any point along the tube by the reversion spectroscope, whilst the time taken for the process is calculated from the velocity of flow of the fluid along the tube, the fluid being in turbulent motion.

In the world in which we now are, this reaction is relatively slow; and, as Fig. 8 shows, it obeys the "rules of the game" inasmuch as the curve obtained by plotting the logarithm of the concentration of the oxyhæmoglobin against the time is a straight line.

The reaction :

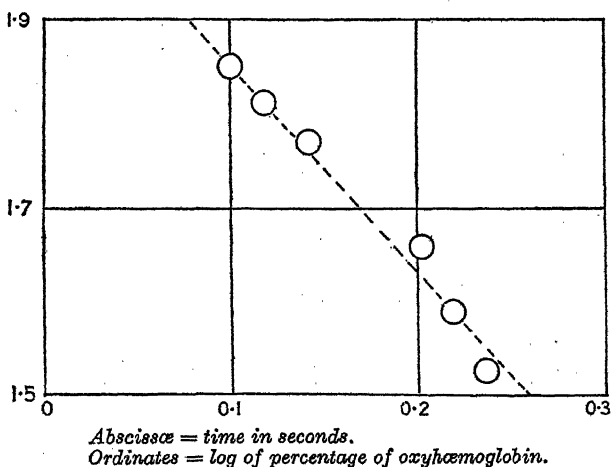


presents much greater difficulties for two reasons. The first is the technical one that it takes place enormously faster, the second is the theoretical one that it has not proved practicable to remove the oxide as it is formed and therefore it is only when the first portions of oxide are forming that the reaction appears with its full velocity. However, just because the disruption of the oxide is slow

as compared with its formation, and because we know the velocity of the disruption, we can correct for it by a process of calculation.

To determine the velocity of oxidation, solutions of hæmoglobin and of oxygen in sufficient concentration to oxidise it are driven at such a velocity that they traverse the lower limbs of the Y at the rate of about 600 cm. per second, and over the first few centimetres the chemical change may be seen with the eye, the hæmoglobin turning from violet to red as the oxide forms. The measurements are made with the reversion spectroscope. The time, as before, is measured by the rate at which the fluid travels from point to point, and the degree of oxidation by spectroscopic examination of the fluid from point to point along the tube.

FIG. 8.



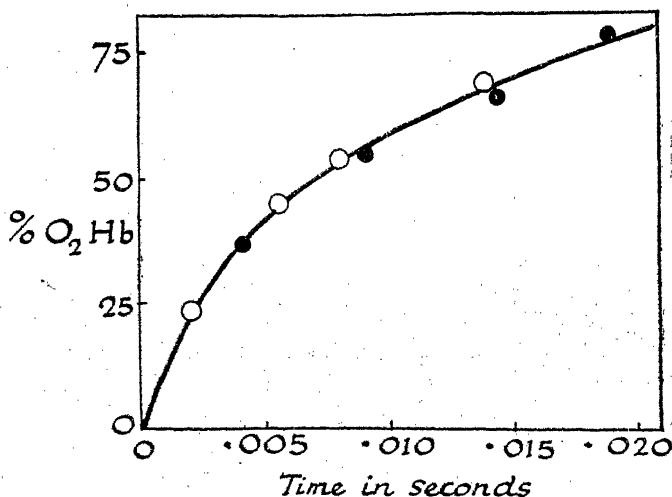
The actual result achieved in an experiment is illustrated by Fig. 9. Here you will see that one-quarter of the whole oxidation takes place in about two-thousandths of a second. To ascertain the figure with an accuracy of but 10% required a certainty of two ten-thousandths of a second in the estimation of the time.

Having said so much about Hartridge and Roughton's method, let me pass to the consideration of their results. Taking first the oxidation, its velocity coefficient possesses properties that are worth noting, the most remarkable of which is that temperature appears to have no effect upon it. Of course I mean temperature within rather narrow limits, for hæmoglobin will not stand heating above about 45°. What the theoretical explanation of this phenomenon may be is a matter which I shall leave to you who know much

more about such things than I do. It would be explained according to the authors on the assumption that all the molecules of oxygen which impinged upon the hæmoglobin molecule—at whatever temperature—adhered to it. The second property, and one which is of great interest to physiologists, is that alteration of the hydrogen-ion concentration of the medium in which the hæmoglobin is dissolved is also without marked effect upon the velocity coefficient of the oxidation phase of the reaction.

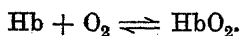
It follows, therefore, that the now well-known effects of hydrogen-ion concentration and temperature on the equilibrium constant must

FIG. 9.



be almost entirely the reflexion of the effects of these conditions on the *reduction* phase, and to this we shall now turn.

Experiments on sheep's hæmoglobin indicate that the velocity coefficient of the reduction phase has a temperature coefficient of 3.8 for an alteration of 10°, which, as a matter of fact, corresponds to that of the equilibrium constant of the reaction

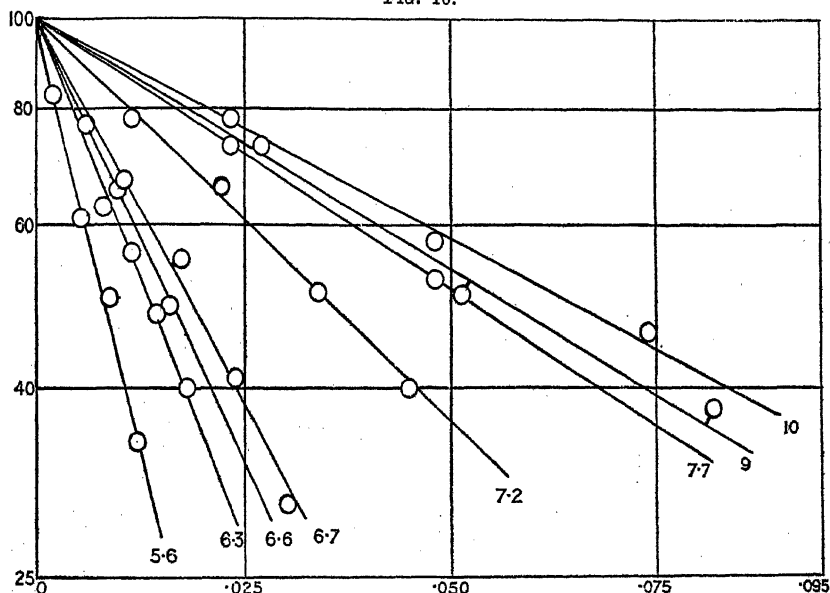


The effect of hydrogen-ion concentration is restricted to a small region between  $p_{\text{H}} = 7.8$  and about  $p_{\text{H}} = 5.5$ , i.e., within 1.2 on each side of the isoelectric point. Within this region the effect is very great and fully accounts for the properties which blood exhibits (Figs. 10 and 11).



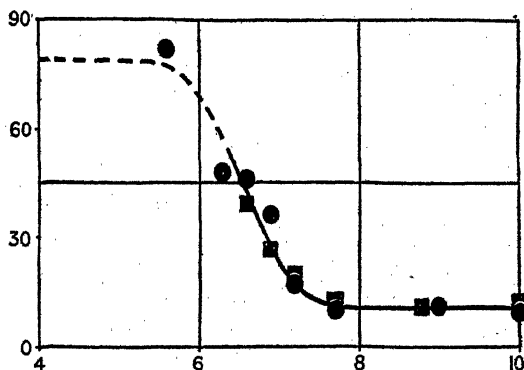
To revert, however, to the original proposition of whether the value of the equilibrium constant as determined does or does not agree

FIG. 10.



*Abscissæ = Time in seconds. Ordinates = logarithm of oxyhaemoglobin percentage; numerals on left of ordinate axis indicate corresponding value of oxyhaemoglobin percentage.*

FIG. 11.



*Abscissæ =  $p_H$  of solution. Ordinates = value of reduction velocity coefficient. Squares represent results obtained in experiment on one sample of blood. Circles represent results obtained in experiment on another sample of blood.*

with the quotient of the velocity coefficients, the following table, which summarises the results of four such comparisons, shows, I

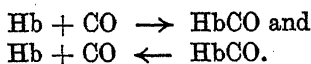
think, as good an agreement as can be looked for from experiments of so high a degree of difficulty.

*The Comparison of K with  $k'/k$ .*

No. of Expt.	$p_{\text{H}}$ .	Temp.	Mean value of $k'$ .	Mean value of $k$ .	Value of $K$ .	
					Calculated from $K = k'/k$ .	Observed from dissociation curve.
I.	7.7	17.5°	2875	17.5	164	218
II.	7.2	18.9	2550	17.3	148	112
III.	10.0	15.1	3145	4.5	700	730
IV.	10.0	17.3	3540	8.1	438	336

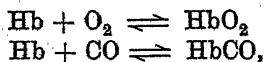
The values of  $k'$ ,  $k$ , and  $K$  were subject individually to possible experimental errors of  $\pm 20\%$ ,  $\pm 10\%$ , and  $\pm 15\%$ , respectively.

A parallel set of observations has been carried out on the velocity coefficient of the reactions

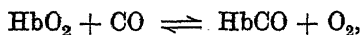


Of these, the velocity coefficient of the association phase is of the same order as that of the corresponding reaction for hæmoglobin and oxygen; but the velocity coefficient of this dissociation phase is of quite a different order from that of the reduction phase of oxy-hæmoglobin.

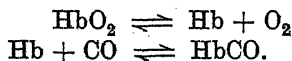
Being in possession of the values of  $k$  and  $k'$  for the reactions



respectively, we should be able to calculate the corresponding coefficients for the reaction



or, as it is more correctly written,



But at this point a most interesting discrepancy has appeared. The hæmoglobin appears to be much more reactive towards carbon monoxide if this gas is presented to it within about one-tenth of a second after the removal of the oxygen than it is subsequently. Whether, in that tenth of a second some tautomeric change takes place, or, if not, what the alternative may be, is still under investigation, so there we must leave the matter.

VI. *The Importance of the Protein.*

Within recent years the point of interest with regard to hæmoglobin has been shifting. Formerly, it was entirely centred upon the relation of the oxygen to the hæmatin, and this interest extended to the significance of the pyrrole group and the possible connexion with chlorophyll. Little progress has been made in this direction; the researches of Willstätter more particularly have turned men's minds rather away from the pyrrole group; on the other hand, the protein moiety of hæmoglobin has in one way or another been steadily receiving more recognition. The points of importance with regard to the protein may be considered under two main groups, those which embrace the proportion of hæmoglobin as an amphoteric electrolyte, and those which have to do with its specificity.

(a) *Hæmoglobin as an Amphoteric Electrolyte.*—Hæmoglobin acts as an acid in alkaline solution and as a base in acid solution. The former action has been studied in much greater detail than the latter. In strict parlance one should, I suppose, speak of hæmoglobinic acid and of sodium or potassium hæmoglobinate—the latter being the form in which hæmoglobin exists for the most part in human blood.

This very important fact at once raises a number of points such as :

( $\alpha$ ) The number of dissociable sodium atoms for each atom of iron.

( $\beta$ ) The strength of the acid.

( $\gamma$ ) Effect on the strength of the acid of oxidising the hæmoglobin.

( $\delta$ ) The repercussion of the above considerations on the system in which hæmoglobin is found in the blood, which contains also sodium bicarbonate, sodium chloride, and carbonic acid. This system becomes complicated by the fact that the hæmoglobin is in corpuscles, the envelopes of which appear to be relatively impermeable to kations as compared with anions. This system is of paramount importance to the physiologist, but to the chemist it is so special a case that I shall pass very lightly over it.

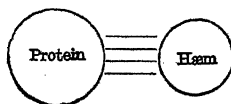
$\alpha$ . Very different views have been held as to the number of gram-atoms of sodium which could dissociate from 16,800 grams of hæmoglobin (the weight which contains 56 grams of iron and unites with 32 grams of dissociable oxygen). The matter recently formed the subject of an exhaustive research by the workers in Dr. Van Slyke's laboratory,<sup>12</sup> who have come to the conclusion that the number was much higher than had formerly been supposed. Their estimate is 12.

$\beta$  and  $\gamma$ . Hæmoglobin in the reduced form is a very weak acid. In the oxidised form it is, according to A. V. Hill, some seventy

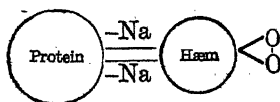
times as strong, and is then of the same order of strength as sodium bicarbonate.

8. It follows that when hæmoglobin is oxidised in the presence of sodium bicarbonate the sodium becomes redistributed, the hæmoglobin taking more, and therefore the amount of sodium bicarbonate decreases whilst the amount of free carbon dioxide increases. On the other hand, the addition to the system of carbon dioxide or any other acid will attract sodium from the hæmoglobin and tend to release the oxygen, which has less affinity for the free acid than for the sodium hæmoglobinate.

The scheme put forward by Hill<sup>13</sup> to explain these facts is that hæmoglobin may be regarded as



whilst oxyhæmoglobin in the presence of sodium bicarbonate is



(b) *Specificity*.—That the hæmoglobins which are derived from different species of animals, and even from different members of the same species, differ may be shown in a number of ways. That they differ in crystalline form has been known for a long time, and the crystallographic differences have formed the subject of a work, monumental in bulk, by Reichert and Brown.<sup>14</sup> Moreover Landsteiner and Heidelberger,<sup>15</sup> in a very elegant research on the solubility of hæmoglobin, have shown that the difference between one form and another is sufficiently great to render them more or less independently soluble. After a solution has been saturated with the hæmoglobin of one animal, it is still capable of dissolving some at all events of the hæmoglobin of another.

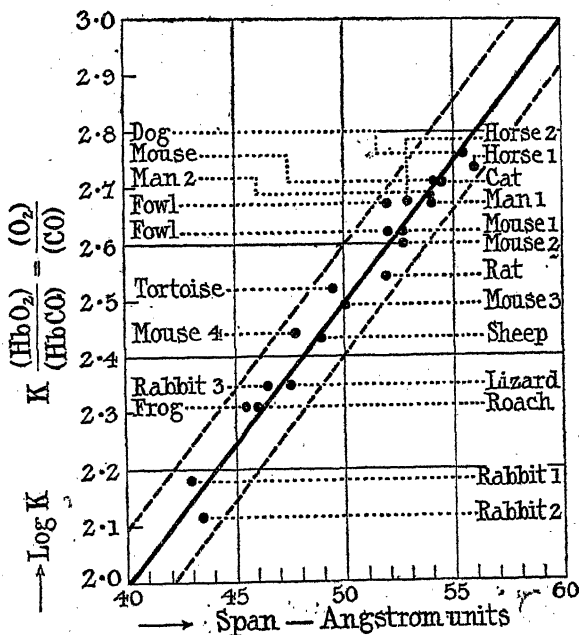
Moreover the spectra are slightly different, the bands being shifted a little towards the red or towards the blue from one hæmoglobin to another. This is true, not only of the bands of oxyhæmoglobin, but also of carboxyhæmoglobin. One band, known as the  $\alpha$ -band, has been studied in some detail. In the case of human blood, when carbon monoxide is bubbled through a solution of oxyhæmoglobin this band moves 54 Å.U. towards the blue. In the slang of the laboratory, we say the band has a "span" of 54 Å.U. Most forms of hæmoglobin have a lesser span. Now let me put before you a remarkable and hitherto unexplained relationship, which at present

exists on quite an empirical basis. It merely has been "observed to be so" in the cases which have been tested.

We may express the equilibrium point of the reaction which takes place when carbon monoxide is passed into oxyhæmoglobin as follows:—<sup>16</sup>



FIG. 12.



With different hæmoglobins,  $K$  differs. Now let me show you the relation of  $K$  to the "span." I do not wish to insist that the relation is in the strict sense linear. We may be on a very flat curve or near the point of inflexion of an S-shaped curve. What I want to emphasise is that *there is a relation*. It would be simple to explain this relation on the hypothesis that there are a limited number of hæmoglobins, say two, which in different animals are mixed together in different proportions. This simple explanation seems to be negatived by the fact that if the hæmoglobin be crystallised and redissolved the solution presents the same properties as the original solution or as the fluid left above the crystals.

On the other hand, no attempt to find any spectroscopic or other differences, either in the hæms or the hæmins derived from these

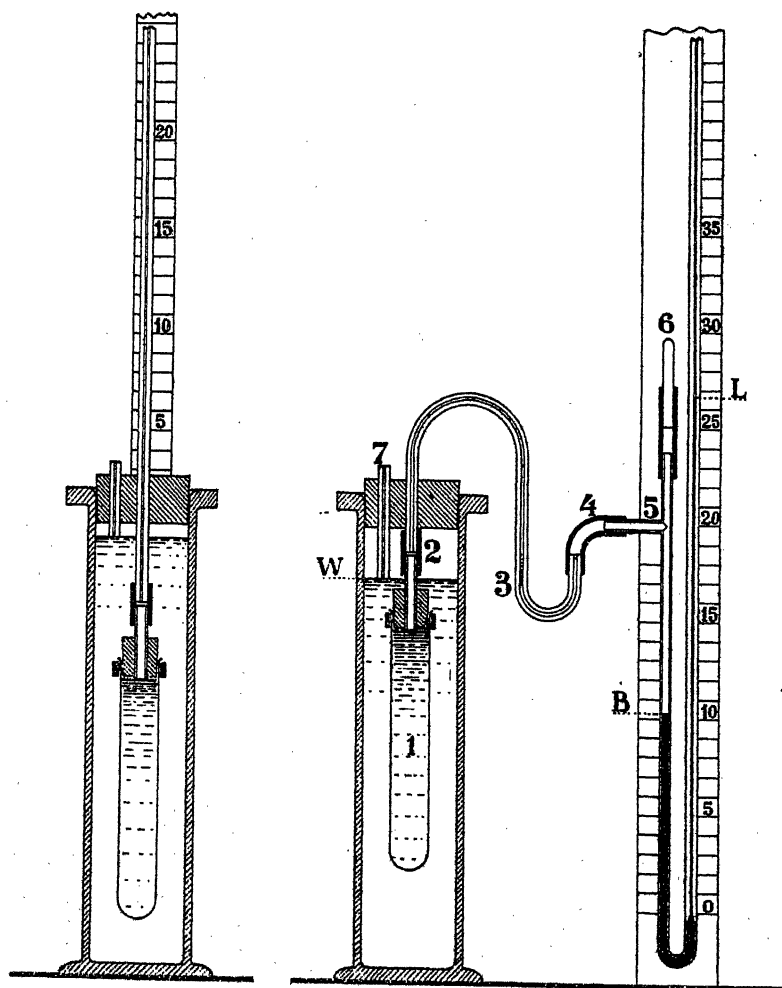
various hæmoglobins, has been successful. In the present state of our knowledge one must attribute this very interesting specific feature to the globins.

### VII. *Osmotic Pressure and Molecular Weight.*

And now I come to that part of the subject in which hæmoglobin appears to be in its most illusive mood. The thing which we most want to know about it is perhaps its molecular weight, and in this audience the confession of ignorance on that point is a confession not untinged with shame. We know as a starting point that the least possible molecular weight—that which contains 56 grams of iron—would be somewhere about 16,700. If then we call the molecular weight  $(16,700)_n$ , what is the value of  $n$ ?

We turn to some indirect method. What is to be said about the osmotic pressure? I may pass rather rapidly over the work of Hüfner and Gansser,<sup>17</sup> who came to the conclusion that the osmotic pressure of a 1% solution of hæmoglobin would be 10 mm. of mercury—a result which would give a value of  $n = 1$ . By what happy accident Hüfner and Gansser arrived at this result is likely to remain a mystery. Weymouth Reid,<sup>18</sup> in a research which is too little quoted, concluded that 3 was the nearest whole number to his determinations of  $n$ . Roaf<sup>19</sup> made the material but rather depressing discovery that  $n$  might appear to be almost anything—less than unity, for instance—according to the circumstances in which the measurements were made. It has remained for Adair<sup>20</sup> to reduce to some sort of order the apparently chaotic readings which were found. The possibilities of adsorbed salts, of variable ionisation of the hydrogen or sodium ions, of membrane potentials, of polymerisation of the hæmoglobin, of the onset of putrefaction, of the attainment of a true equilibrium, etc., all had to be taken into account. Take the last two considerations, the attainment of equilibrium and the avoidance of putrefactive changes. In ordinary circumstances it proved quite impossible to complete a measurement in which a satisfactory equilibrium was attained before the solution ceased to be above suspicion. This difficulty was overcome by working at  $0.6^\circ$ , at which temperature a hæmoglobin solution remains good indefinitely. The time factor looms almost as large in Adair's determinations as in those of Hartridge and Roughton. The latter measure events which take place in a fraction of  $1/1000$  of a second; Adair's osmometric determinations each require a fraction of a year. The work is being carried on in the Low Temperature Station at Cambridge, where Sir Wm. Hardy kindly allows Adair to set up his osmometers (Fig. 13). Such work must be very slow, but already enough information has been

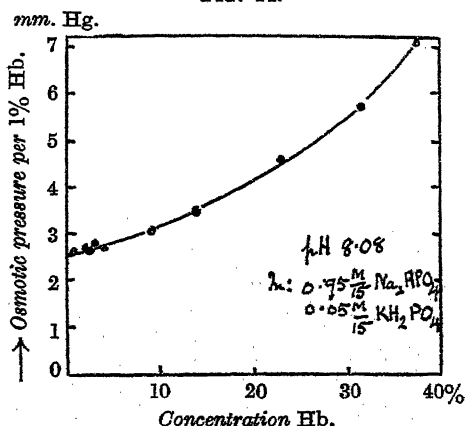
FIG. 13.



Osmometer, Type D (left), with straight column of solution for measuring pressure. Scale in centimetres. Osmometer, Type O (right), for high pressures with mercury manometer: (1) A rigid collodion tube, 20 c.c. capacity, in jar holding 500 c.c. of outer liquid. (2) Rubber connexion. The glass tube from (2) to (3) is filled with liquid paraffin. Beyond (3) there is water. (4) Rubber connexion with clip (not shown here). (5) Glass T tube, with water down to level B. (6) Glass rod in rubber tube, for adjusting the pressure. (7) Glass tube, open to air, or fitted with a soda-lime tube. W = level of outer liquid; B = level of mercury in manometer limb, 6 mm. in diameter; L = level of mercury in manometer limb, 0.7 mm. in diameter. Above the mercury at L there is a drop of lactic acid.

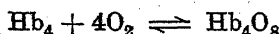
obtained to be of considerable interest. Adair will show you a model in which the osmotic pressure in a 1% solution of hæmoglobin is represented vertically whilst the hydrogen-ion concentration and the saline concentration of the solvent are the horizontal co-ordinates. Over a great part of this model the conditions may be varied without any change in the osmotic pressure of the hæmoglobin, which pressure works out pretty regularly at 2.6 mm. of mercury. This figure is given if the solution is not more than 4% hæmoglobin or is not of less saline concentration than 0.01 molar. Where a different and higher osmotic pressure than 2.6 is given per 1% of hæmoglobin, as in cases where the concentration of Hb is more than 4% (Fig. 14)

FIG. 14.



or the pigment is dissolved in salt solution of greater dilution than 0.01M (Fig. 15), Adair finds a cause which satisfies him. If we accept his estimate, the value of  $n$  would be 4 and the molecular weight of hæmoglobin about 68,000. A substance of this molecular weight, it may be said incidentally, would depress the freezing point of water about 0.00001°.

And now we are face to face with the final puzzle. How are we to reconcile an equation

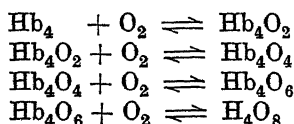


with the form of equilibrium curve as obtained?

In considering this question I will leave out two factors each of which may produce an appreciable secondary effect on the shape of the curve. These are the alteration in hydrogen-ion concentration produced on oxidation and the effect of the great concentration in

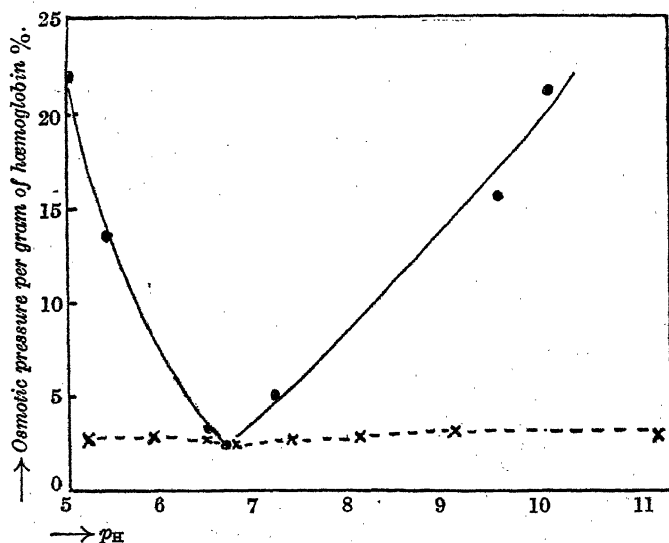


which the hæmoglobin is found, say, in the red corpuscle. These apart, we may consider the reaction as being either



or it may follow what physiologists call the "all or none" principle, there being no possibility of intermediate oxides between  $\text{Hb}_4$  and

FIG. 15.



Conditions. Concentration of Hb less than 4%.

o Solution in distilled water.

x Solution of saline concentration greater than 0.01M.

$\text{Hb}_4\text{O}_8$ . The latter hypothesis yields a curve of the S-shaped form with which we are familiar in the case of blood.

In the case of successive oxidations, if the equilibrium constants of the four reactions are in the ratios of 4 : 3 : 2 : 1, i.e., if each oxygen may be regarded as of the same value and uninfluenced by the presence or absence of the others, a curve of the hyperbolic form would be produced such as has been obtained in the case of carbon monoxide and a dilute solution of hæmoglobin of relative purity. It may here be remarked that the "all or none" conception may be

regarded as a special case of the conception of successive oxides, the case in which the equilibrium constants of the intermediate oxides have not got finite values, and that being so, it is possible to produce any curve of the general type given by the equation

$$y/100 = Kx^n/(1 + Kx^n),$$

where  $n$  is between 1 and 4, by suitably arranging the equilibrium constants of the successive reactions. But we have now passed entirely into the domain of speculation. We know of no reason why the actual factors which do alter the inflexion of the curve should so affect the equilibrium constants of the successive oxidation equilibria, and no one has claimed to have isolated any of the intermediate oxides, or to have obtained anything but the most nebulous evidence of their existence.

Yet so long as the physical basis of the inflexion fails to be understood the dream of the physiologist will be unfulfilled, for the inflexion of the curve is the biologically important fact about it. One day the enigma will be solved, until then we can but strive on in the sure and certain hope that "Nature never has betrayed the heart that loved her."

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- <sup>3</sup> Keilin, *Proc. Roy. Soc.*, 1925, B, 97, 312.
- <sup>4</sup> R. Hill, *Biochem. J.*, xix.
- <sup>5</sup> C. Bohr, *Z. Physiol.*, 1903, 17, 690.
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- <sup>13</sup> A. V. Hill, *Biochem. J.*, 1922, 51, 359.
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- <sup>15</sup> Landsteiner and Heidelberger, *J. Gen. Physiol.*, 1923, 6.
- <sup>16</sup> Anson, Barcroft, Mirsky, and Oinuma, *Proc. Roy. Soc.*, 1924, B, 97, 61.
- <sup>17</sup> Hüfner and Gansser, *Arch. Anat. Physiol.*, 1907, p. 209.
- <sup>18</sup> Reid, *J. Physiol.*, 1904, 31, 438; 1905, 33, 12.
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CL.—*A Theory of Colour on the Basis of Molecular Strain. The Effect of Chromophoric Superposition.*

By SIKHIBHUSHAN DUTT.

THE visible colour of substances is due to selective absorption of certain of the electro-magnetic vibrations causing the sensation of white light and the transmission of the remainder. In the present paper an attempt is made to show that selective absorption is due to molecular strain, such strain being imparted to the molecule by the distortion of the normal valency directions produced by any of the following causes :

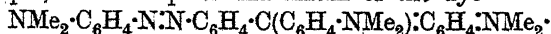
- (a) Formation of a double or triple bond.
- (b) Formation of a cyclic from an open-chain compound.
- (c) Unequal distribution of the masses attached to the atom.

The amount of strain is roughly proportional to the angular displacements of the valency directions of the atoms.

Strain in a molecule can be intensified by loading, the greatest effect being obtained when the load is in close proximity to the centre of strain. The farther the load is from this centre, the less is its effect.

The effect produced when two sources of strain are in close proximity in a molecule is much greater than that produced when they are remote from each other, because in the former case the intervening single linking also assumes a comparatively strained condition, thereby increasing the total rigidity of the molecule. The two strains produce the greatest effect when they originate in the same atom ; they have scarcely any mutual effect, each operating independently of the other, when they are situated at atoms separated by more than one single linking.

The position of the absorption maximum of a dye, the molecule of which contains two different and distantly situated chromophores, is approximately the mean of the positions of the maxima of the two components of the dye, each containing one chromophore. For example, the absorption maximum of the dye



is at  $\lambda$  5570, and those of its components, benzeneazodimethylaniline and malachite-green, are at  $\lambda$  5040 and  $\lambda$  6190 respectively (mean,  $\lambda$  5615). A dye containing several chromophores of the same kind has almost the same absorption maximum as the dye containing only one such chromophore. Hence, in each of these two cases, the effects of the strains, situated in distant positions in the molecule, are independent of each other.

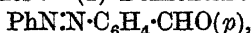
## EXPERIMENTAL.

*Azotriphenylmethane Dyes. Series I. Dyes containing One or Two Azo-groups attached to One Benzene Nucleus.*

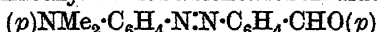
These dyes were obtained by oxidising the leuco-bases formed by condensing mono- and bis-azobenzaldehydes with dimethylaniline.

*Preparation of Azobenzaldehydes.*—The following mono- and bis-azobenzaldehydes were prepared by diazotising the substance named first in the bracket and coupling the product with the second-named substance. *p*-Aminobenzaldehyde was diazotised as described in D.R.-P. 85233 of 1895, and *m*-aminobenzaldehyde in concentrated hydrochloric acid. The coupling with phenol was done in 10% sodium hydroxide solution. The coupling with aniline or dimethylaniline was done in a mixture of concentrated hydrochloric and glacial acetic acids, which were thereafter gradually neutralised with sodium carbonate.

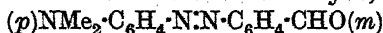
Monoazobenzaldehydes: (1) Benzeneazobenzaldehyde,



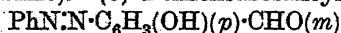
prepared by the method described in Beilstein's "Organische Chemie," Vol. IV, p. 1068. (2) *p*-Hydroxybenzeneazobenzaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$  (*p*-aminobenzaldehyde; phenol). (3) *p*-Dimethylaminobenzeneazobenzaldehyde,



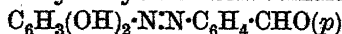
(*p*-aminobenzaldehyde; dimethylaniline). (4) *p*-Aminobenzeneazobenzaldehyde,  $(p)\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$  (*p*-aminobenzaldehyde; aniline). (5) *p*-Hydroxybenzeneazo-*m*-benzaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(m)$  (*m*-aminobenzaldehyde; phenol). (6) *p*-Dimethylaminobenzeneazo-*m*-benzaldehyde,



(*m*-aminobenzaldehyde; dimethylaniline). (7) *p*-Aminobenzeneazo-*m*-benzaldehyde,  $(p)\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(m)$  (*m*-aminobenzaldehyde; aniline). (8) Benzeneazosalicylaldehyde,

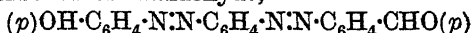


(aniline; salicylaldehyde). This substance is identical with the compound prepared by Borsche (*Ber.*, 1900, 33, 1325) from benzeneazophenol, chloroform, and sodium hydroxide. (9) *p*-Hydroxybenzeneazosalicylaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_3(\text{OH})(p)\cdot\text{CHO}(m)$  (*p*-aminophenol hydrochloride; salicylaldehyde). (10) *p*-Methoxybenzeneazobenzaldehyde,  $(p)\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$ , prepared by treating (2) with methyl sulphate and 3% sodium hydroxide solution. (11) 2:4-Dihydroxybenzeneazobenzaldehyde,



(*p*-aminobenzaldehyde; resorcinol). (12) 2:3:4-Trihydroxybenzeneazobenzaldehyde,  $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{N:N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(p)$  (*p*-aminobenz-

aldehyde; pyrogallol). Bisazobenzaldehydes: (13) *p*-Hydroxybenzeneazobenzeneazobenzaldehyde,



(No. 4, diazotised as described in D.R.-P. 85233; phenol).

(14) *p*-Dimethylaminobenzeneazobenzeneazobenzaldehyde,



(No. 4; dimethylaniline). (15) *p*-Hydroxybenzeneazobenzeneazo-*m*-benzaldehyde,  $(p)\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}(m)$  (No. 7, diazotised in concentrated hydrochloric acid; phenol). (16) *p*-Dimethylaminobenzeneazobenzeneazo-*m*-benzaldehyde,



(No. 7; dimethylaniline).

No diazoamino-compound was formed in the preparation of substances 4 and 7.

Substances 2, 11, 12, and 13 were crystallised from glacial acetic acid, and substances 3—8, 10, and 14—16 from alcohol. Substance 9 separated in an amorphous form from acetic acid.

Some properties of the azo-aldehydes are given in Table I.

TABLE I.  
*Azobenzaldehydes.*

Azo-aldehyde.	Appearance.	M. p.	N % (theor. % in brackets).
2	Golden-yellow spangles with metallic lustre.	199°	12.5 (12.3)
3	Glistening, red prisms.	170	16.9 (16.6)
4	Yellowish-brown prisms.	158	18.5 (18.7)
5	Orange-yellow prisms.	164—165	12.2 (12.3)
6	Brownish-yellow needles.	116	16.8 (16.6)
7	Yellow prisms.	85—87	18.3 (18.7)
8	Golden-yellow needles.	128	12.1 (12.3)
9	Dark brown powder.	117—120	11.9 (11.6)
10	Bright yellow needles.	130—131	11.4 (11.7)
11	Microscopic, red needles.	Above 300	11.2 (11.6)
12	Microscopic, brown needles.	„	11.1 (10.8)
13	Glistening, brownish-yellow needles.	190	17.3 (16.9)
14	Dark red needles.	142—143	19.2 (19.6)
15	Glistening orange-yellow prisms.	135	16.7 (16.9)
16	„ „ „	128—129	19.8 (19.6)

*General Method of Condensation of Azobenzaldehydes with Dimethylaniline, and Preparation of the Corresponding Azotriphenylmethane Dyes.*—A solution or suspension of the azobenzaldehyde (1 mol.) and dimethylaniline (2 mols.) in ten times their volume of a mixture of equal parts of concentrated hydrochloric and glacial acetic acids was heated under reflux for periods of time varying from 3 to 12 hours, the end of the reaction being shown by the production of a clear solution and the change in colour from dark red to pale yellow.

The solution was poured into water, made alkaline with sodium carbonate, and every trace of dimethylaniline removed by distillation in steam. The white precipitate of the leuco-base was dissolved in dilute hydrochloric acid and reprecipitated from the filtered solution with sodium carbonate. In most cases the leuco-base could not be further purified or crystallised, owing to oxidation, and was therefore directly oxidised to the dye.

The oxidation was carried out by heating a solution of the leuco-base in sufficient 50% acetic acid with slightly more than the theoretical quantity of freshly precipitated and moist manganese dioxide (prepared by quantitative precipitation of potassium permanganate in warm water with alcohol) on the steam-bath for about 1 hour, with frequent stirring. After filtration, the solution of the colouring matter was treated with excess of saturated sodium acetate solution, and the precipitated dye was washed with water, dried, and crystallised from various solvents such as chloroform-ligroin, benzene, acetic acid, alcohol, and acetone, chloroform-ligroin (1 : 2) being the best solvent for the purpose. The substances thus obtained were acetates of the corresponding carbinol bases, and crystallised in glistening prisms or leaflets with a coppery lustre. They are generally sparingly soluble in water or benzene, moderately easily soluble in dilute mineral acids, alcohol, acetone, or acetic acid, very soluble in chloroform or pyridine, and insoluble in ligroin. They dye wool in various shades, from reddish-violet to deep blue.

*Series II. Azotriphenylmethane Dyes containing Two Azo-groups attached to Two Benzene Nuclei.*

Dyes of this series were prepared by tetrazotising *pp'*-diaminotriphenylmethane and its substitution products, coupling the products with dimethylaniline (2 mols.) in the usual manner, and oxidising the leuco-bases thus formed.

1. *pp'*-Diaminotriphenylmethane,  $\text{CHPh}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , was obtained by O. Fischer's method (*Annalen*, 1881, **206**, 147).

2. *p*-Hydroxy-*p'**p''*-diaminotriphenylmethane,  
 $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ .

—An intimate mixture of *p*-hydroxybenzylideneaniline (1 mol.), aniline hydrochloride (1 mol.), and concentrated hydrochloric acid (5 mols.) was heated in a sealed tube for 6 hours. The product was diluted with water, filtered, and the filtrate rendered alkaline with sodium carbonate solution. The resulting white precipitate, after being washed with water, crystallised from pyridine-alcohol in colourless needles, not melting at  $295^\circ$ . It dissolved very easily in dilute acids to pale yellow solutions, and was found to contain

two amino-groups by titration with  $N/2$ -sodium nitrite (Found: N, 9.3.  $C_{19}H_{18}ON_2$  requires N, 9.7%).

3. *p*-Dimethylamino-*p*'*p*''-diaminotriphenylmethane,



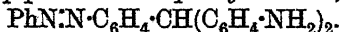
—*p*-Dimethylaminobenzaldehyde (5 g.), aniline (7 g.), and strong hydrochloric acid (50 c.c.) were boiled under reflux for about 5 hours. The leuco-base was isolated as in the above instance. It crystallised from alcohol in colourless leaflets, m. p. 152°. It was very soluble in dilute acids and was found to contain two amino-groups by the standard method (Found: N, 13.6.  $C_{21}H_{23}N_3$  requires N, 13.2%).

*General Method of Preparation of the Dyes of this Series.*—The diaminotriphenylmethane (1 mol.) in excess of dilute hydrochloric acid was treated with sodium nitrite (2 mols.), and the tetrazo-solution added to dimethylaniline (2 mols.) dissolved in strong hydrochloric or glacial acetic acid. On gradual neutralisation of the acid with sodium carbonate, the azo-dye separated. After being washed and crystallised from alcohol or glacial acetic acid, the leuco-base in hot glacial acetic acid was oxidised to the carbinol by freshly precipitated manganese dioxide in the usual manner. The dyes thus obtained are yellow, but the leuco-bases are brown. They dissolve in concentrated hydrochloric acid with a pink colour, whilst in ordinary solvents the colour is yellow.

*Series III. Azotriphenylmethane Dyes containing Three Azo-groups attached to Three Benzene Nuclei.*

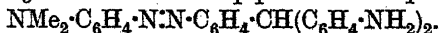
These dyes were obtained by tetrazotising *p*-benzeneazo-*p*'*p*''-diaminotriphenylmethane and its substituted derivatives, and coupling the products with dimethylaniline in the usual way. The leuco-bases thus obtained are unaffected by oxidation. In behaviour they are all similar to simple azo-dyes like benzeneazodimethylaniline. They are all yellow, but dissolve in concentrated hydrochloric acid with a red colour.

1. *p*-Benzeneazo-*p*'*p*''-diaminotriphenylmethane,



—This substance was obtained by heating benzeneazobenzaldehyde (1 mol.) with aniline (2 mols.) and concentrated hydrochloric acid (10 mols.) in a sealed tube at 200° for 6 hours. It crystallises from alcohol in brownish-yellow needles, m. p. 174°, and is very easily soluble in dilute acids (Found: N, 14.5.  $C_{25}H_{22}N_4$  requires N, 14.8%).

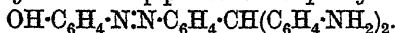
2. *p*-4-Dimethylaminobenzeneazo-*p*'*p*''-diaminotriphenylmethane,



—*p*-Dimethylaminobenzeneazobenzaldehyde (6 g.), 5 g. of aniline,

30 c.c. of strong hydrochloric acid, and 20 c.c. of glacial acetic acid were heated under reflux for about 3 hours until the colour of the solution had changed from dark crimson to pale yellow. The solution was poured into water and made alkaline with sodium carbonate; the precipitate produced, after being filtered off, washed and dried, crystallised from benzene in brownish-yellow needles, m. p.  $165^{\circ}$  (Found: N, 17.0.  $C_{27}H_{27}N_5$  requires N, 16.6%).

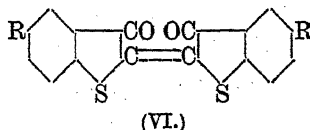
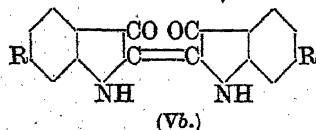
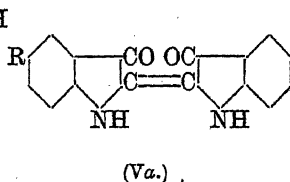
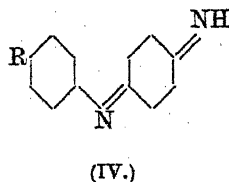
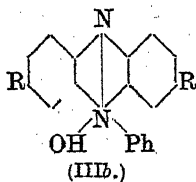
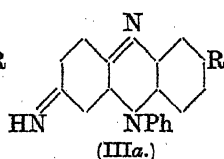
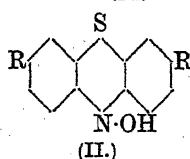
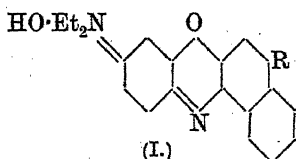
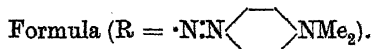
3. *p*-4-Hydroxybenzeneazo-*p*'*p*''-diaminotriphenylmethane,



—This substance was prepared from *p*-hydroxybenzeneazobenzaldehyde (1 mol.) and aniline (2 mols.) in a similar way to the above. It crystallised from alcohol in yellow aggregates, m. p.  $162$ – $163^{\circ}$  (Found: N, 14.5.  $C_{25}H_{22}ON_4$  requires N, 14.2%).

*Series IV. Dyes containing Different Kinds of Chromophores.*

For the preparation of the following dyes of the mixed type, all the diazotisations or tetrazotisations were carried out in cold strong sulphuric acid solution with the theoretical quantities of sodium nitrite. The sulphuric acid solutions were then diluted with ice-water and coupled with the required quantities of dimethylaniline in the usual manner:



(1) Azo-oxazine dye: *Nile-blue-2-azodimethylaniline* (formula I), from diazotised Nile-blue A; dark violet, microscopic needles from chloroform-benzene (N found, 15.4; theo., 14.9%).

(2) Azo-thiazine dye: *Lauth's violet-2:7-bisazodimethylaniline*



(II), from tetrazotised Lauth's violet; brownish-yellow powder from pyridine (N found, 19.7; theo., 19.2%).

(3) Azo-safranine dyes: (a) *Safranine-2-azodimethylaniline* (IIIa), from diazotised phenosafranine hydrochloride; dark violet needles from alcohol (N found, 20.4; theo., 20.1%). (b) *Safranine-2:7-bisazodimethylaniline* (IIIb), from tetrazotised phenosafranine hydrochloride; brownish-yellow needles from alcohol (N found, 19.3; theo., 19.7%).

(4) Azo-indamine dye: *Indamine-3-azodimethylaniline* (IV), from diazotised phenylene-blue; violet, microscopic needles from chloroform (N found, 21.5; theo., 21.3%).

(5) Azo-indigoid dyes: (a) *Indigotin-5-azodimethylaniline* (Va), from diazotised 5-aminoindigotin; violet needles with silky lustre from pyridine (N found, 17.3; theo., 17.1%). (b) *Indigotin-4:4'-bisazodimethylaniline* (Vb), from tetrazotised 4:4'-diaminoindigotin (*Monatsh.*, 1905, 62, 1262); brownish-yellow, microscopic needles from acetic acid (N found, 19.3; theo., 19.2%).

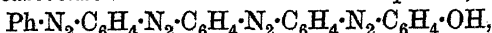
(6) Azo-thioindigoid dye: "*Thioindigo*"-5:5'-*bisazodimethylaniline* (VI), from tetrazotised 5:5'-diaminothioindigo (D.R.-P. 240805); light brown, amorphous powder (N found, 14.5; theo., 14.2%).

#### *Series V. Reduplication of the Same Chromophore.*

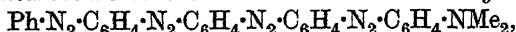
A. *The Azo-group.*—1. *Benzeneazobenzeneazobenzeneazoaniline*,  $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ . *Benzeneazobenzeneazoaniline* (*Ber.*, 1888, 21, 2145) (1 mol.) was diazotised in cold concentrated hydrochloric acid solution, and the product coupled with phenol (1 mol.), dissolved in excess of sodium hydroxide, in the usual manner. The final product crystallised from glacial acetic acid in bright yellow prisms, m. p. 248° (Found: N, 20.4.  $\text{C}_{24}\text{H}_{18}\text{ON}_6$  requires N, 20.7%).

2. *Benzeneazobenzeneazobenzeneazoaniline*,  
 $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ,  
 was obtained by coupling diazotised *benzeneazobenzeneazoaniline* (1 mol.) with aniline (1 mol.) dissolved in the minimum quantity of strong hydrochloric acid and, after thorough stirring, adding an excess of sodium acetate. The product crystallised from alcohol in yellow leaflets, m. p. 194°. No diazoamino-compound was formed (Found: N, 24.4.  $\text{C}_{24}\text{H}_{19}\text{N}_7$  requires N, 24.2%).

3. *Benzeneazobenzeneazobenzeneazodimethylaniline*,  
 $\text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ ,  
 was prepared in a similar way to the above by using dimethylaniline in place of aniline. It crystallised from alcohol in orange leaflets, m. p. 218° (Found: N, 22.8.  $\text{C}_{26}\text{H}_{23}\text{N}_7$  requires N, 22.6%).

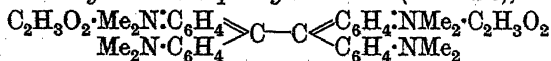
4. *Benzeneazobenzeneazobenzeneazobenzeneazophenol*,

was obtained by diazotising benzeneazobenzeneazobenzeneazoaniline (1 mol.) in cold strong sulphuric acid solution and coupling the product with phenol (1 mol.), dissolved in excess of sodium hydroxide, in the usual way. It crystallised from nitrobenzene in brownish-yellow prisms, not melting at  $290^\circ$  (Found: N, 22.3.  $\text{C}_{30}\text{H}_{22}\text{ON}_8$  requires N, 22.9%).

5. *Benzeneazobenzeneazobenzeneazodimethylaniline*,

was prepared by adding diazotised benzeneazobenzeneazobenzeneazoaniline (1 mol.) to dimethylaniline (1 mol.), dissolved in concentrated hydrochloric acid, and, after thorough stirring, adding an excess of sodium acetate. It crystallised from pyridine in orange-yellow prisms, not melting at  $290^\circ$  (Found: N, 23.2.  $\text{C}_{32}\text{H}_{27}\text{N}_9$  requires N, 23.4%).

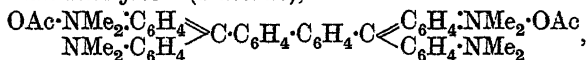
B. *The Diphenylmethane Group*.—1. *Bistetramethyldiaminodiphenylmethane*,  $(\text{NMe}_2 \cdot \text{C}_6\text{H}_4)_2\text{CH} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ . A mixture of 10 g. of glyoxal, 22 g. of dimethylaniline, and 50 c.c. of fuming hydrochloric acid was heated in a sealed tube at  $180^\circ$  for 8 hours. The product was diluted with water, rendered alkaline with sodium carbonate, and distilled in steam until no more dimethylaniline passed over. The residue, which solidified on cooling, was ground up, washed with water, and its solution in dilute hydrochloric acid was decolorised by boiling with animal charcoal and sulphurous acid. The filtered solution on treatment with dilute sodium hydroxide gave a white precipitate of the leuco-base, which was filtered off, washed, and dried on a porous plate; it crystallised from ether in colourless needles, m. p.  $96-98^\circ$ , which became brownish-violet on exposure to air (Found: N, 11.4.  $\text{C}_{34}\text{H}_{42}\text{N}_4$  requires N, 11.1%).

2. *Bistetramethyldiaminodiphenylcarbinol (diacetate)*,

The above leuco-base was dissolved in sufficient 50% acetic acid, slightly more than the calculated quantity of freshly precipitated manganese dioxide added, and the mixture thoroughly stirred. The solution, dark green at first, on warming on the steam-bath became brilliant violet-blue. After heating for about an hour, it was filtered, cooled, and treated with an excess of saturated sodium acetate solution. The precipitated colouring matter was filtered off, washed, and dried; it crystallised from chloroform-ligroin in dark violet-blue needles with a coppery lustre which dissolved in organic solvents and dilute acids with a violet-blue colour (Found: N, 9.3.  $\text{C}_{38}\text{H}_{46}\text{O}_4\text{N}_4$  requires N, 9.0%).

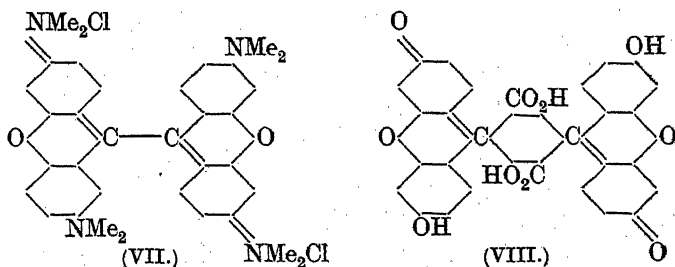
C. *The Triphenylmethane Group*.—1. *leuco-Dimalachite-green*,  $(\text{NMe}_2\cdot\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ . *p*-Bromoleucomalachite-green [m. p.  $128^\circ$ , obtained from *p*-bromobenzaldehyde (1 mol.) and dimethylaniline (2 mols.), concentrated hydrochloric acid at  $200^\circ$  being used as the condensing agent] was intimately mixed with an equal weight of very fine copper bronze, and the mixture heated at  $210$ – $220^\circ$  in an atmosphere of hydrogen. In 1 hour, a reaction took place which was indicated by the loss of metallic lustre of the bronze powder. After heating for about 4 hours, the melt was dissolved in dilute hydrochloric acid, the solution filtered, the filtrate decolorised with animal charcoal and sulphur dioxide, and the leuco-base precipitated with dilute sodium hydroxide. It could not be crystallised and was a white powder, m. p.  $135$ – $138^\circ$ , which readily became green on exposure to air (Found: N, 8.2.  $\text{C}_{46}\text{H}_{50}\text{N}_4$  requires N, 8.5%).

2. *Dimalachite-green (diacetate)*,



prepared by oxidising the above leuco-base with manganese dioxide, could not be crystallised and was obtained as a brilliant green powder which dissolved in organic solvents and dilute acids with a deep green colour (Found: N, 7.6.  $\text{C}_{50}\text{H}_{54}\text{O}_4\text{N}_4$  requires N, 7.2%).

D. *The Pyronine Group*.—*Dipyrone G* (formula VII). Glyoxal (1 mol.), dimethyl-*m*-aminophenol (4 mols.), and strong hydrochloric acid (10 mols.) were heated together on the steam-bath for about 12 hours under reflux in a current of carbon dioxide. The product was diluted with water, and the leuco-base precipitated with sodium carbonate. As it could not be purified in this state, being very easily oxidised in the air, it was repeatedly dissolved in dilute hydrochloric acid and reprecipitated with sodium carbonate before being converted into the dye. This conversion was done by dissolving the leuco-base in cold strong sulphuric acid and adding

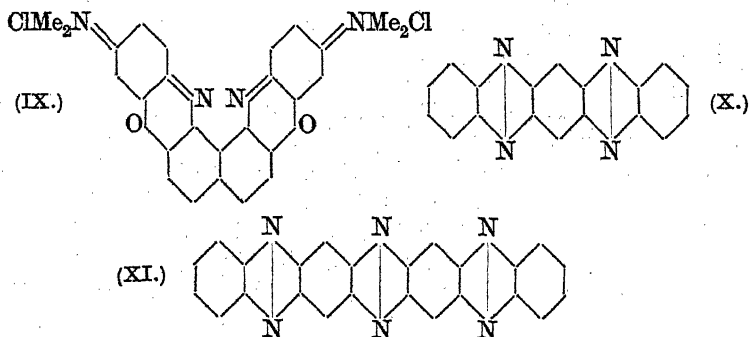


slightly more than the calculated quantity of sodium nitrite, with vigorous stirring. The solution became dark red and small steel-  
s s\*

blue needles began to separate. After 1 hour, the solution was poured into ice-water, and the dye precipitated by adding a concentrated solution of sodium chloride. It came down in fine steel-blue needles with a golden iridescence, and was filtered off, washed with a little water, and dried. Its solutions in water and in organic solvents have a brilliant pink colour (Found : N, 9.6.  $C_{34}H_{36}O_2N_4Cl_2$  requires N, 9.3%).

E. *The Phthalein Group.*—*Difluorescein* (VIII) was obtained by condensing pyromellitic acid with-resorcinol (4 mols.) according to the method (J., 1906, 89, 1787) by which the corresponding compound was prepared from mellitic acid. It is a dark yellow, amorphous substance, not melting at  $300^\circ$  (Found : C, 69.5; H, 3.4.  $C_{34}H_{18}O_{10}$  requires C, 69.6; H, 3.0%).

F. *The Oxazine Group.*—*Di-Meldola's blue* (IX). *p*-Nitrosodimethylaniline hydrochloride ( $4\frac{1}{2}$  mols.) and 2 : 7-dihydroxynaphthalene (1 mol.) were heated together in alcoholic solution under reflux for 24 hours. The black crystalline colouring matter that had separated was filtered off, washed with alcohol and water, and dried. It was a black, crystalline powder, dissolving in organic solvents with a dark green colour (Found : N, 11.6.  $C_{26}H_{22}O_2N_4Cl_2$  requires N, 11.3%).



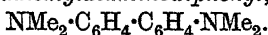
G. *The Azine Group.*—1. *Phenazineazine* (X) was obtained by condensing 2 : 3-diaminophenazine (Ber., 1889, 22, 356) with *o*-benzoquinone in concentrated sulphuric acid solution. It crystallises from nitrobenzene, and also sublimes on careful heating, in bright yellow needles which do not melt at  $290^\circ$  (Found : N, 19.7.  $C_{18}H_{10}N_4$  requires N, 19.8%).

2. *Phenazineazineazine* (XI) was obtained by condensing 2 : 3-diaminophenazine with 2 : 3-dihydroxyphenazine (Ber., loc. cit.) in cold strong sulphuric acid solution containing 30% of sulphur trioxide. It crystallises from nitrobenzene in microscopic yellow

needles which do not melt at  $290^{\circ}$  (Found: N, 21.6.  $C_{24}H_{12}N_6$  requires N, 21.8%).

*Series VI.*

*A. Malachite-green with a Bridge Linking between Two Benzene Nuclei.*—1. 3 : 3'-Tetramethyldiaminodiphenyl,





3 : 3'-Dinitrodiphenyl (*Ber.*, 1901, **34**, 2177) was reduced with tin and hydrochloric acid in the usual way, the tin precipitated with hydrogen sulphide, and the filtered solution evaporated to dryness. The hydrochloride of 3 : 3'-diaminodiphenyl, thus obtained in long, colourless, silky needles, was dissolved (10 g.) in 150 c.c. of water, and 60 g. of methyl sulphate were added, about 5 g. at a time with vigorous shaking, during an hour, the solution being neutralised from time to time with 10% sodium hydroxide solution; methylation was complete when excess of sodium hydroxide failed to precipitate any amino-compound. The yellow crystalline chromate of the quaternary base precipitated from this solution by a strong aqueous solution of chromic acid was filtered off, washed with water, and treated in aqueous suspension with sulphur dioxide. The dark green solution thus obtained was boiled to drive off the excess of sulphur dioxide and rendered strongly alkaline with ammonia, the precipitated chromium hydroxide washed with water, and the filtrate and washings were evaporated to dryness. The residue was extracted with absolute alcohol, and the extract, after being distilled on the steam-bath until no more alcohol came over, was heated at  $250^{\circ}$  in a vacuum for  $\frac{1}{2}$  hour; only a small, pale yellow distillate, however, was obtained. The distillate and the residue were dissolved in hot dilute hydrochloric acid and the solution was decolorised with animal charcoal. From the filtered solution dilute aqueous sodium hydroxide precipitated a solid, which crystallised from alcohol in clusters of colourless needles, m. p.  $126-128^{\circ}$ , easily soluble in dilute mineral acids (Found: N, 11.5.  $C_{16}H_{20}N_2$  requires N, 11.8%).

2. *The leuco-base, 3 : 6-tetramethyldiamino-9-phenylfluorene (XII).* A solution of 3 : 3'-tetramethyldiaminodiphenyl (1 mol.) and benzal chloride (1 mol.) in dry carbon disulphide was heated under reflux with powdered anhydrous aluminium chloride (2 mols. plus 10% excess) for about 6 hours. The carbon disulphide was distilled off, the dark brown aluminium compound decomposed with water, and the white residue filtered, washed, and extracted with very dilute acetic acid (in which 3 : 3'-tetramethyldiaminodiphenyl is insoluble). The extract was rendered alkaline with sodium carbonate, and the precipitated leuco-base filtered off and washed with

TABLE II.

*Absorption Maxima of Azotriphenylmethane Dyes.*

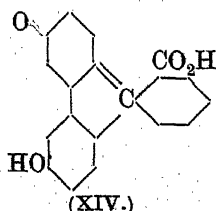
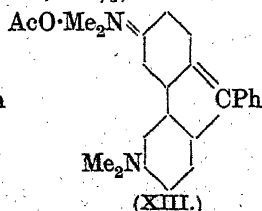
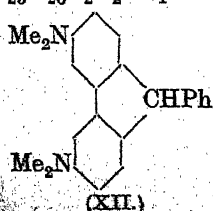
The dye whose symbolical formula is in the first column was prepared from the aldehyde, the reference number of which is in the second column.  $\alpha$  denotes the absorption maximum of the dye in alcoholic solution containing 1 mol. of HCl, and in the last column are its found and theoretical (in brackets) percentages of nitrogen. A =  $C_6H_5 \cdot N \cdot N \cdot$  or  $\cdot C_6H_4 \cdot N \cdot N \cdot$ , B =  $C_6H_5$  or  $C_6H_4$ , etc., C = methane carbon atom, and R and R' respectively =  and

::NMe<sub>2</sub>·OAc.

Formula.	Aldehyde.	$\alpha$ .	N %.
B·C:RR' (malachite-green).	—	6190	—
A·B (azobenzene).	—	4310	—
A·R (butter-yellow).	—	5040	—
A·B·C:RR'.	I, 1	5720	11·5 (11·2)
(4)HO·B·A·C:RR'.	I, 2	5560	11·3 (11·0)
(4)HO·B·C:RR'.	—	5960	(J., 1917, 111, 815)
(4)HO·B·A·A·C:RR'.	I, 13	5580	14·1 (13·7)
(2:4)(HO) <sub>2</sub> B·C:RR'.	—	6010	(J., <i>ibid.</i> )
(2:4)(HO) <sub>2</sub> B·A·C:RR'.	I, 11	5650	11·0 (10·7)
(2:3:4)(HO) <sub>3</sub> B·C:RR'.	—	6120	(J., <i>ibid.</i> )
(2:3:4)(HO) <sub>3</sub> B·A·C:RR'.	I, 12	5670	10·8 (10·4)
R·C:RR' (crystal-violet).	—	5990	—
R·A·C:RR'.	I, 3	5570	13·4 (13·0)
R·A·A·C:RR'.	I, 14	5580	15·8 (15·3)
(3)HO·B·C:RR' (patent blue).	—	6010	7·1 (6·9)
(4)HO·B·(1)A·(3)C:RR'.	I, 5	5650	11·8 (11·0)
(4)HO·B·A·(1)A·(3)C:RR'.	I, 15	5730	14·0 (13·7)
(2)HO·B·(1)C:RR'.	—	5990	7·2 (6·9)
$\frac{A(4)}{HO(2)} > B(1)C:RR'$ .	I, 8	5570	11·9 (11·8)
(4)MeO·B·C:RR'.	—	6050	(Ber., 1881, 14, 2523)
(4)MeO·B·A·C:RR'.	I, 10	5610	10·9 (10·7)
$\frac{(1)HO \cdot A(4)}{HO(2)} > B(1)C:RR'$ .	I, 9	5650	11·1 (10·7)

water. It could not be crystallised and melted at 92—94° (Found: N, 8·7.  $C_{23}H_{24}N_2$  requires N, 8·5%).

3. *The dye (acetate) (XIII).* The above leuco-base was oxidised in 50% acetic acid solution with freshly precipitated manganese dioxide in the usual manner. It was obtained from chloroform-ligroin as a dark green, crystalline powder, which formed dark green solutions in organic solvents and dilute acids (Found: N, 7·5.  $C_{25}H_{26}O_2N_2$  requires N, 7·2%).



B. *Phenolphthalein with a Bridge across two Benzene Nuclei (XIV).*

—A mixture of 9 g. of 3:3'-dihydroxydiphenyl (Ber., 1894, 27,

2107), 7.5 g. of phthalic anhydride, and 15 g. of anhydrous aluminium chloride was heated at 200° for 5 hours. The product was powdered, extracted with boiling water, the residue dissolved in hot aqueous sodium carbonate, the solution filtered, and the filtrate acidified; the dye was thus obtained in pale purple flocks. It crystallised from glacial acetic acid (animal charcoal) in colourless needles, not melting at 285°. It dissolved in alkalis with a bluish-red colour (Found: C, 75.7; H, 4.0.  $C_{20}H_{12}O_4$  requires C, 75.9; H, 3.7%).

TABLE III.

*Absorption Maxima of Azotriphenylmethane Dyes (Series II and III).*

These dyes were prepared by tetrazotising the amines referred to in the second column, coupling the products with dimethylaniline (2 mols.), and oxidising the final products.  $\alpha$  is now the absorption maximum of the dye in conc. HCl.

Formula.	Amine.	$\alpha$ .	N %.
B·C(OH):(A·R) <sub>2</sub> .	II, 1	5050	15.5 (15.1)
(4)OH·B·C(OH):(A·R) <sub>2</sub> .	II, 2	5140	15.1 (14.7)
R·C(OH):(A·R) <sub>2</sub> .	II, 3	5160	16.1 (16.4)
B·A·CH:(A·R) <sub>2</sub> .	III, 1	5070	17.8 (17.4)
(4)OH·B·A·CH:(A·R) <sub>2</sub> .	III, 3	5070	17.5 (17.0)
R·A·CH:(A·R) <sub>2</sub> .	III, 2	5070	18.2 (18.3)

TABLE IV.

*Absorption Maxima of Azo-dyes of the Mixed Type (Series IV).*

Name or reference.	Absorption maxima ( $\lambda$ ).	Name or reference.	Absorption maxima ( $\lambda$ ).
Nile-blue A.....	6040	Indigotin .....	6050
IV, 1 .....	5820	5-Aminoindigotin .....	5890
Lauth's-violet .....	5970	IV, 5a .....	5720
IV, 2 .....	5050	4 : 4'-Diaminoindigotin...	5940
Phenylene-blue .....	6600	IV, 5b .....	5010
IV, 4 .....	5980	"Thioindigo" .....	5240
Phenosafranine .....	5250	5 : 5'-Diaminothioindigo	5230, 5920
IV, 3a .....	5790	IV, 6 .....	4990
IV, 3b .....	5130		

*Absorption Maxima of Dyes with Reduplicated Chromophores (Series V).*

Benzeneazophenol .....	4330	Malachite-green .....	6190
Benzeneazobenzeneazo-phenol .....	4350	V, C 2 .....	6220
V, A 1 .....	4360	Pyronine .....	5380 (6670)
V, A 4 .....	4360	V, D .....	5380 (6680)
Benzeneazodimethyl-aniline .....	5040	Meldola's blue .....	6060
Benzeneazobenzeneazodimethylaniline .....	5090	V, F .....	7020
V, A 3 .....	5130	Phenazine .....	4290
V, A 5 .....	5140	V, G 1 .....	4310
Michler's hydrol .....	6080	V, G 2 .....	4320
V, B 2 .....	5990	Fluorescein .....	4940
		V, E .....	4950
		VI, A 3 .....	6210
		Phenolphthalein .....	5540
		VI, B .....	5550

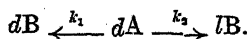
My best thanks are due to Professor J. F. Thorpe, F.R.S., for the kind interest he has taken in this work, to Professor A. Fowler, F.R.S., for permission to use his quartz spectrograph, and to the Chemical Society for a grant which has defrayed part of the expense of this research.

IMPERIAL COLLEGE, SOUTH KENSINGTON. [Received, October 30th, 1925.]

# CLI.—*Studies on the Walden Inversion. Part X.* *The Reaction between Water and the Phenylchloro- acetate and Phenylbromoacetate Ions.*

By ALLAN MILES WARD.

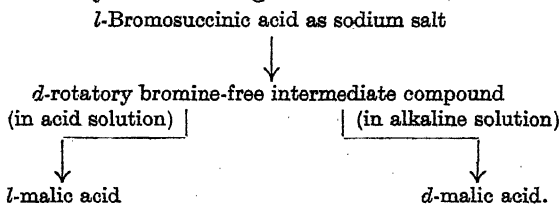
RACEMISATION may be effected by two processes apparently distinct, namely (1) without displacement of groupings, and (2) during group-displacement. Catalytic racemisation falls under case (1). The generally accepted mechanism of (1) is that the racemisation is due either (*a*) to a tautomeric change, or (*b*) to an equilibrium existing between the original substance and the products formed by its dissociation, one of which is unsaturated at the asymmetric centre (compare Lowry, *Rep. Brit. Assoc.*, 1904; McKenzie and Widdows, *J.*, 1915, **107**, 702; McKenzie and Wren, *J.*, 1919, **115**, 602; Walden, "Optische Umkehrerscheinungen," 1919, V Kapitel). By such a mechanism the resulting mixture of optical isomerides, if not quite inactive, must contain an excess of the isomeride initially present, a Walden inversion thus being impossible. This statement, however, would not be applicable in the case of asymmetric catalytic racemisation (McKenzie and Smith, *Ber.*, 1925, **58**, 894). On the other hand, racemisation of type (2) may be effected by the occurrence of two simultaneous reactions, whereby both *d*- and *l*-isomerides of the product are formed as follows:



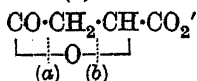
The two reactions, which may be identical from the ordinary kinetic standpoint, proceed with velocities, the coefficients of which,  $k_1$  and  $k_2$ , may be equal or different. The relative values of  $k_1$  and  $k_2$  might vary largely according to the experimental conditions, so that in some cases  $k_2$  would be negligible in comparison with  $k_1$ , when only one isomeride would result. When  $k_1$  and  $k_2$  become equal, the product would be entirely racemic; whilst, depending on the relative values of  $k_1$  and  $k_2$ , a complete range of intermediate activities of either sign is possible. By such a mechanism a Walden inversion may thus be effected. This view has been suggested in



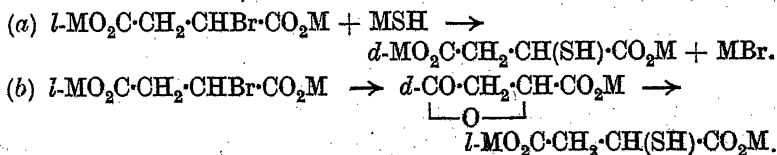
various forms many times previously (compare Fischer, *Annalen*, 1911, 381, 126; Werner, *ibid.*, 1912, 386, 68), and the experiments of Holmberg, whereby active products of either sign are produced from a given initial material, provide a proof for the case in which the mechanisms of the production of the two isomerides differ when deduced from the ordinary kinetic standpoint. Thus the kinetic results (Holmberg, *J. pr. Chem.*, 1913, 87, 456) show that the conversion of sodium or silver *l*-bromosuccinate into malic acid proceeds through an intermediate stage, since definitely established as malolactone. If this reaction is carried out in acid solution, the product from *l*-bromosuccinic acid is *r*- and *l*-malic acids, whilst in alkaline solution *r*- and *d*-malic acids are formed. Holmberg represented this by the following scheme:



This scheme closely resembles the one used above, but the mechanism of the production of the malic acids from the lactone is not discussed, and appears to be more allied to Phillips's investigations (J., 1923, 123, 22; Kenyon, Phillips, and Turley, J., 1925, 127, 399; Phillips, *ibid.*, p. 2563) than to the present work, the reaction probably taking place by the fission of one or other of the bonds in malolactone as indicated in positions (a) and (b)

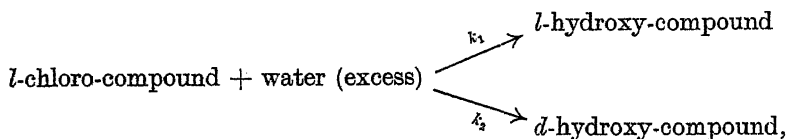


In the subsequent experiments on the xanthosuccinic acids and the thiolmalic acids (Holmberg, *J. pr. Chem.*, 1913, 88, 553; *Arkiv Kemi, Min., Geol.*, 1916, 6, No. 1; 1916, 6, No. 8; Holmberg and Lenander, *ibid.*, 1917, 6, No. 17) evidence from kinetic results shows the reaction to proceed both by direct substitution of the halogen and also *via* the lactone, and from experiments with the reactants in various concentrations, the following mechanism was put forward for the conversion into the thiolmalic acids (and similarly for the xanthosuccinic acids):



The mechanisms for the production of the stereoisomeric thiolmalic acids (and xanthosuccinic acids) are here kinetically different, whereas in the present investigation the mechanisms are the same from the ordinary kinetic point of view.

Considered on a quantitative basis, the reaction (*e.g.*)



in order to fulfil the conditions of the above mechanism, must (from the results of kinetic measurements) be one of a simple order, and the value of  $k$  thus calculated will be equal to  $k_1 + k_2$ , whilst, from the results of measurements of the change of rotation of the solution of the active substance with time under the same conditions as employed for the inactive, the same value of  $k$  should result. To test these considerations the conversion of sodium *l*-phenylchloroacetate into sodium *r*- and *l*-mandelate has been carried out. The action of water on *l*-phenylchloroacetic acid, of water on sodium *l*-phenylchloroacetate, and of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate was first studied by McKenzie and Clough (J., 1908, 93, 811; 1909, 95, 777), who found that the mandelic acid produced was laevorotatory and that extensive racemisation occurred in these changes. The kinetics of the conversion of *r*-phenylchloroacetic acid and its sodium salt in aqueous solution, and also of the sodium salt in aqueous caustic soda solution, have been investigated (Senter, J., 1915, 107, 908), and it was shown that each of the above reactions is one and the same, namely, the reaction of water with the phenylchloroacetate ion. The best value for the velocity coefficient for the conversion of sodium *r*-phenylchloroacetate in aqueous sodium hydroxide solution at 25° was considered to be 0.00146, where time is measured in minutes, but the values of  $k$  actually found (*loc. cit.*, p. 914) at 25° for the sodium salt ( $N/10$ ) were

(a) in caustic soda ( $N/10$ ), 0.00138, 0.00142, 0.00145,

(b) „ „, ( $N/5$ ), 0.00134, 0.00134, 0.00138.

Thus the reaction here dealt with is  $\text{PhCHCl}\cdot\text{CO}_2' + \text{H}_2\text{O}(\text{excess}) \rightarrow \text{PhCH}(\text{OH})\cdot\text{CO}_2' + \text{NaCl}$  from the kinetic point of view. Table I gives the results of the corresponding polarimetric experiment, which was carried out as follows. To 150 c.c. of aqueous sodium hydroxide (0.1858*N*) at 24–85° were added 2.3037 g. of *l*-phenylchloroacetic acid with  $[\alpha]_{\text{D}}^{25} = -191.5^\circ$  in benzene (resolved by the method of McKenzie and Clough, *loc. cit.*, except that the morphine salt was

decomposed by dilute aqueous ammonia). The acid rapidly dissolved to a clear, colourless solution, which was maintained at 24.85°. Samples were withdrawn at the times shown in Table I, and their rotations determined, using a 2-dcm. tube and the yellow mercury line.

TABLE I.

Time.	$\theta_t$ (obs.).	$\theta_t$ (calc.).	$k$ .	
			Differential.	Integral.
0 mins.	-[4.52]			
7	4.50			
39	4.24	-4.25	0.0019	0.00168
61	4.12	4.11	0.0013	0.00156
121	3.75	3.74	0.0016	0.00158
181	3.38	3.33	0.0018	0.00165
240	3.05	3.10	0.0018	0.00169
300	2.82	2.83	0.0014	0.00162
360	2.55	2.58	0.0018	0.00164
420	2.35	2.35	0.0014	0.00161
480	2.15	2.14	0.0016	0.00160
543	2.00	1.95	0.0012	0.00156
600	1.76	1.79	0.0024	0.00164
665	1.59	1.62	0.0017	0.00164
730	1.50	1.47	0.0010	0.00158
1510	0.54	0.50	0.0013	0.00154
1773	0.38	0.36	0.0017	0.00157
2037	0.26	0.28	0.0022	0.00166
2931	0.16	0.15	0.0011	0.00153
5 days	0.11			
8	0.10			
17	0.11			
Mean			0.0016	Mean 0.00161

The values of  $k$  differential (column 4) are obtained from the formula

$$k = \frac{\delta\theta}{\delta t} \cdot \frac{2}{\theta_{t_2} + \theta_{t_1} - 2\theta_\infty}$$

where  $\theta_{t_2}$  and  $\theta_{t_1}$  are consecutive observations,  $\delta\theta = \theta_{t_2} - \theta_{t_1}$  and  $\delta t = t_2 - t_1$ . The values of  $k$  thus calculated are irregular, as is only to be expected, since a small error in the determination of  $\theta$ , causes, by this method, a large variation in the coefficient. No drift in value, however, occurs, and the applicability to this case is thus shown of the integrated form (column 5) for a unimolecular reaction, namely,  $k = \frac{2.3}{t} \log_{10} \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$ .

This method of calculation does, however, suffer from the defect that great importance is placed on the value of  $\theta_0$ , but the mean value of  $k$  obtained by both methods is substantially the same. A duplicate determination using an acid with  $[\alpha]_{D^{780}} - 188^\circ$  gave  $k = 0.00160$ .

It would thus appear that the mechanism is in the main as postulated, but the divergence between the values of the coefficients

as thus calculated and those of Senter (*loc. cit.*) remains to be accounted for. The following experiment on sodium *l*-mandelate showed that under the conditions of the preceding experiments mandelic acid does not undergo catalytic racemisation, at least with any speed comparable with that of the displacement here studied. To 1.3865 g. of *l*-mandelic acid with  $[\alpha]_{D}^{15} - 159^\circ$  in water, was added a mixture of 50 c.c. of sodium chloride (0.2020*N*) and 50 c.c. of aqueous sodium hydroxide (0.1858*N*) at 24.85°. The solution was maintained at this temperature, and samples were withdrawn at intervals and their rotations determined, the yellow mercury line and a 2-dcm. tube being used. The results are shown below:

Time (hours)	0.10	2.05	12.05	30.5	50.0	3 days	9 days
Rotation ...	-3.25°	-3.43°	-3.35°	-3.43°	-3.44°	-3.44°	-3.44°

Thus no contributory factor here arises to produce the difference in the two values. There remains the slight possibility that the coefficient for sodium *l*-phenylchloroacetate is not the same as that for sodium *r*-phenylchloroacetate, but this was disposed of by carrying out experiments (a) and (b) below.

(a) To 1.4822 g. of *l*-phenylchloroacetic acid, with  $[\alpha]_{D}^{24} - 188^\circ$  at 24.85°, were added 100 c.c. of sodium hydroxide (0.2010*N*). Samples of 10 c.c. were withdrawn at times shown, and titrated against sulphuric acid ( $1.037 \times N/20$ ), phenolphthalein being used as indicator.

(b) This experiment was carried out simultaneously with (a), and the conditions were identical, except that 1.5816 g. of *r*-phenylchloroacetic acid were used.

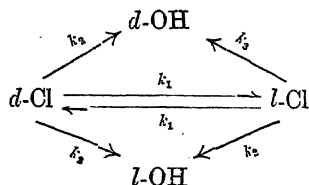
The results are in Table II, *k* being equal to  $2.3/t \cdot \log_{10} a/(a-x)$ .

TABLE II.

<i>l</i> -Acid.			<i>r</i> -Acid.		
Time.	Titre.	<i>k</i> .	Time.	Titre.	<i>k</i> .
3 mins.	21.45		4 mins.	20.43	
60	20.38		60	19.13	
120	18.22	0.00128	180	16.84	0.00126
360	15.42	0.00131	360	13.89	0.00129
540	13.31	0.00129	540	11.57	0.00130
660	12.03	0.00131	660	10.20	0.00133
1500	7.41	0.00131	1500	5.10	0.00138
4 days	5.09		6 days	2.87	
Mean 0.00130			Mean 0.00131		

It thus appears certain there is a divergence between the values of *k* as determined from titres and from optical measurements, and this may be satisfactorily accounted for by assuming that, in addition to the displacement racemisation of the phenylchloro-

acetate ion, there is a simultaneous catalytic racemisation of this ion, so that the completed scheme would become:



If  $a$  is the initial concentration of  $d$ -chloro-compound,  $b$  the initial concentration of  $l$ -chloro-compound,  $x$  and  $y$  the amounts of  $d$ - and  $l$ -chloro-compounds respectively changed in time  $t$ ,

$$\text{then } dx/dt = k_1(a - x) - k_1(b - y) + (k_2 + k_3)(a - x) \quad (1)$$

$$\text{and } dy/dt = k_1(b - y) - k_1(a - x) + (k_2 + k_3)(b - y) \quad (2)$$

Integration of (1) and (2) gives

$$x = a - \frac{a+b}{2} e^{-(k_2+k_3)t} - \frac{a-b}{2} e^{-(2k_1+k_2+k_3)t} \quad (3)$$

$$\text{and } y = b - \frac{a+b}{2} e^{-(k_2+k_3)t} + \frac{a-b}{2} e^{-(2k_1+k_2+k_3)t} \quad (4)$$

For the hydroxy-compounds, if  $w_d$  and  $w_l$  are the concentrations of  $d$ - and  $l$ - forms, respectively, present at time  $t$ ,

$$\text{then } dw_d/dt = k_2(a - x) + k_3(b - y) \quad (5)$$

Substituting in (5) the values of  $x$  and  $y$  in (3) and (4) and integrating

$$\begin{aligned}
 w_d = & -\frac{a+b}{2} e^{-(k_2+k_3)t} - \frac{k_2-k_3}{2k_1+k_2+k_3} \cdot \frac{a-b}{2} \cdot e^{-(2k_1+k_2+k_3)t} \\
 & + \frac{(k_1+k_2)a + (k_1+k_3)b}{2k_1+k_2+k_3}
 \end{aligned}$$

Similarly

$$\begin{aligned}
 w_l = & -\frac{a+b}{2} e^{-(k_2+k_3)t} - \frac{k_3-k_2}{2k_1+k_2+k_3} \cdot \frac{a-b}{2} \cdot e^{-(2k_1+k_2+k_3)t} + \\
 & \frac{(k_1+k_3)a + (k_1+k_2)b}{2k_1+k_2+k_3}
 \end{aligned}$$

Thus at any time  $t$ , the observed rotation of the solution ( $\theta_t$ ) is equal to the rotation of the chloro-compounds + the rotation of the hydroxy-compounds, i.e.,  $\theta_t = D_{CH}(a - x) - (b - y) + D_{OH}(w_d - w_l)$ , where  $D_{CH}$ ,  $D_{OH}$  are the rotations of unit concentrations

of *d*-chloro- and *d*-hydroxy-compounds, respectively, under the given conditions, *i.e.*,

$$\theta_t = D_{Cl}(a-b)e^{-(2k_1+k_2+k_3)t} + D_{OH} \cdot \frac{(k_2-k_3)(a-b)}{2k_1+k_2+k_3} \{1 - e^{-(2k_1+k_2+k_3)t}\}.$$

In the present case,  $a = 0$ , so that

$$\theta_t = -D_{Cl} \cdot b \cdot e^{-(2k_1+k_2+k_3)t} - D_{OH} \cdot b \cdot \frac{k_2-k_3}{2k_1+k_2+k_3} \{1 - e^{-(2k_1+k_2+k_3)t}\} \quad (6)$$

To evaluate  $k_1$ ,  $k_2$  and  $k_3$ , we have from (6) when  $t = 0$ ,

$$\theta_0 = -D_{Cl} \cdot b = -4.52 \text{ (Table I)} \quad . \quad . \quad . \quad (7)$$

and when  $t = \infty$ ,

$$\theta_\infty = -D_{OH} \cdot b \cdot \frac{k_2-k_3}{2k_1+k_2+k_3} = -0.11 \text{ (Table I).}$$

Substituting in (6),

$$\begin{aligned} \theta_t &= -4.52e^{-(2k_1+k_2+k_3)t} - 0.11 + 0.11e^{-(2k_1+k_2+k_3)t} \\ &= -4.41e^{-(2k_1+k_2+k_3)t} - 0.11, \end{aligned}$$

$$\text{i.e.,} \quad e^{(2k_1+k_2+k_3)t} = \frac{-4.41}{\theta_t + 0.11} = \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty},$$

$$\text{therefore} \quad 2k_1 + k_2 + k_3 = \frac{2.3}{t} \log_{10} \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} = 0.00161 \text{ (Table I)}$$

and  $k_2 + k_3 = 0.00130$  (Table II), so that  $k_1 = 0.000155$ .

Further, from the data on p. 1188, 2.054 g. of mandelic acid ( $= 2.3037$  g. of phenylchloroacetic acid) have rotation  $-3.39^\circ = -D_{OH} \cdot b$ .

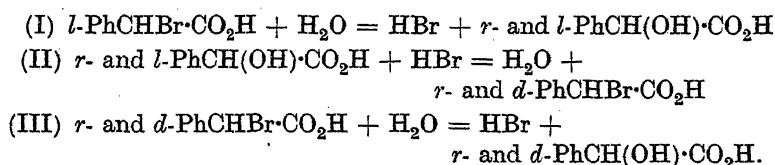
Therefore from (7),  $-0.11 = -3.39 \frac{k_2-k_3}{0.00161}$ , so that  $k_2 - k_3 = 0.000052$ , whence  $k_2 = 0.000676$  and  $k_3 = 0.000624$  and  $\theta_t = -4.41e^{-0.00161t} - 0.11$ .

For comparison with the observed values of  $\theta_t$ , those values thus calculated are shown in column 3, Table I.

The divergence between the coefficients from the corresponding titration and optical experiments is thus satisfactorily accounted for by assuming that besides the displacement racemisation, there is also a catalytic racemisation.

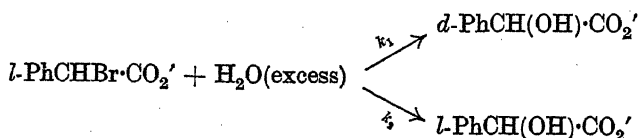
It becomes of interest to review in the same way the results of McKenzie and Walker (J., 1915, 105, 1685) on the conversion of *l*-phenylbromoacetic acid and its sodium salt in aqueous and aqueous caustic soda solutions, in conjunction with the corresponding kinetic experiments of Senter and Tucker (J., 1916, 107, 690). The experiments of Senter and Tucker on the reactions between *l*-phenylbromoacetic acid and its sodium salt, and also

between aqueous caustic soda and sodium *r*-phenylbromoacetate, showed that the main reaction in each case consists of the interaction of water and the phenylbromoacetate ion, exactly as for phenylchloroacetic acid. From the results on the bromo-acid, it was considered that in this case water also reacts with the undissociated acid, the reaction between water and the ion being some 120 times faster than between water and the undissociated acid. The main reaction here dealt with is, therefore,  $\text{PhCHBr}\cdot\text{CO}_2' + \text{H}_2\text{O}(\text{excess}) \rightarrow \text{PhCH}(\text{OH})\cdot\text{CO}_2'$ . As for the chloro-acid, the rate of reaction is thus dependent on the hydrogen-ion concentration, and development of hydrogen ions during the reaction causes a marked falling off in the value of the velocity coefficient. McKenzie and Walker found in some of their experiments that the reaction between water and *l*-phenylbromoacetic acid gave *d*- and *r*-mandelic acids, whilst in other cases *l*- and *r*-acids resulted, and to account for this the following scheme was put forward (*loc. cit.*, p. 1689):



The changes of rotation involved in the cases on which this theory is based were very small. Thus from the data in Table I (*loc. cit.*, p. 1693) the change is from  $-0.02^\circ$  to  $+0.04^\circ$ . Assuming that the *l*-rotation due to the mandelic acid when (I) is complete is  $-0.02^\circ$ , if no racemisation at all took place in (II) and (III), then the rotation of the *d*-mandelic acid would be  $+0.02^\circ$ , and could not be  $+0.04^\circ$  by this mechanism, although a difference of  $\pm 0.02^\circ$  is within the limits of experimental error. If, however, it is assumed that (II) and (III) proceed at all, extensive racemisation would undoubtedly accompany both stages, so that for practical purposes the resultant mandelic acid would be optically inactive. Furthermore, these processes must be assumed to continue indefinitely, and by the above mechanism complete racemisation must ultimately result, but in the first experiment quoted (*loc. cit.*, p. 1692), the mandelic acid isolated after 3 weeks had  $\alpha_D + 0.16^\circ$ ,  $[\alpha]_D + 4.7^\circ$ , whilst in the second experiment, the mandelic acid isolated after two months at  $25^\circ$  had  $\alpha_D + 0.31^\circ$ ,  $[\alpha]_D + 5.2^\circ$ . It does not appear justifiable to base any accurate comparison on the third experiment (*loc. cit.*, p. 1692), in which an optically impure phenylbromoacetic acid ( $[\alpha]_D - 70^\circ$ ) was used, when it was found that the rotation of the solution before isolation of the product was  $\alpha_D - 0.16^\circ$ , and of the mother-liquors after isolation was  $\alpha_D - 0.45^\circ$ ; the rotation of

the mandelic acid isolated (= 18.2% of theory) is not recorded, and the rotations of the solutions in this case might well be due to some impurity present initially in the partly racemic phenylbromoacetic acid used. Thus it does not appear that McKenzie and Walker's scheme is correct. Also no explanation is apparent for the almost complete racemisation in stage (I). On the other hand, if the mechanism of the reaction is assumed in the main to be



where  $k_1$  and  $k_2$  are nearly equal, closer agreement between theory and experiment is obtained. In some cases, according to the conditions,  $k_1$  may be greater than  $k_2$ , corresponding with the production of a final dextrorotation, whilst if  $k_1$  is less than  $k_2$ , then the solution will remain levorotatory. This explanation is only tenable if the change of sign of rotation is in accord with the displacement effect as determined by titration, and whereas McKenzie and Walker's experiments showed the displacement to be complete before a final steady rotation value was obtained, the following experimental results did not confirm this.

*Reaction between Water and r-Phenylbromoacetic Acid at 25°.*

Water (250 c.c.) was added to *r*-bromo-acid (1.3438 g. =  $N/40$  and 2.5088 g. =  $1.867N/40$ , respectively); in the case of the  $N/40$  solution, 72 minutes elapsed before the solution was homogeneous, whilst for the  $1.867N/40$  solution, 173 minutes were required. These times are reckoned as zero in each set of results. Samples (10 c.c.) were withdrawn and titrated against sodium hydroxide solution (1.011 $N/40$ ), with phenolphthalein as indicator. The results are in Table III,  $k_1$  and  $k_2$  being calculated from the usual unimolecular formula.

The theoretical final titres are 19.78 c.c. and 36.93 c.c., respectively. The above data confirm the results of Senter and Tucker (*loc. cit.*, p. 694) and McKenzie and Walker (*loc. cit.*, p. 1693) that the value of the velocity coefficient in  $N/40$  solution is appreciably higher than in  $1.867 \times N/40$  solution (McKenzie and Walker state their results as  $k \times 10^{-3}$ , whereas they should be  $k \times 10^{-2} \times 2.3$ ). This difference is in accord with the different relative concentrations of phenylbromoacetate ions in the two solutions, for, in the reactions

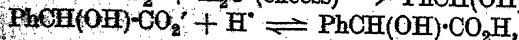
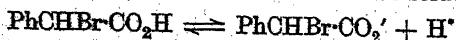




TABLE III.

N/40.			1.867 × N/40.		
Time.	Titre.	$k_1$ .	Time.	Titre.	$k_2$ .
0 mins.	12.7		0 mins.	25.5	
15	13.3	0.00596	15	26.3	0.00480
30	13.9	0.00626	30	27.0	0.00465
60	14.2	0.00401	60	27.5	0.00318
90	15.0	0.00442	90	28.1	0.00284
120	15.5	0.00425	120	28.6	0.00261
150	15.9	0.00407	150	29.2	0.00258
180	16.2	0.00385	180	29.9	0.00268
210	16.6	0.00388	210	30.4	0.00264
240	16.9	0.00381	240	30.7	0.00251
270	17.1	0.00366	270	31.3	0.00260
330	17.5	0.00350	330	31.8	0.00240
390	17.8	0.00334	390	32.0	0.00213
450	18.1	0.00328	450	32.5	0.00208
510	18.4	0.00330	510	32.9	0.00202
570	18.6	0.00324			
25 hrs.	19.3		24 hrs.	36.0	
47	19.7		45½	37.0	
72	19.7		70½	37.0	

if  $a_1$  is the initial concentration of bromo-acid and  $\alpha_1$  the degree of dissociation, the initial concentration of phenylbromoacetate ion is  $a_1\alpha_1$  and therefore the initial rate of reaction is  $k\alpha_1a_1$ , whereas the rate in Table III is actually measured by  $k_1a_1$ , so that  $k = k_1/\alpha_1 = k_2/\alpha_2$  similarly. Now  $\alpha_1 = 0.3106$  for N/40-solution, since the dissociation constant for phenylbromoacetic acid is 0.0035 (Senter and Tucker, *loc. cit.*, p. 692) and  $k_1 = 0.00406$ , taking the mean value in Table III (since the initial values are irregular), so that  $k = 0.013$ . Similarly for 1.867N/40-solution,  $\alpha_2 = 0.2390$  and  $k_2 = 0.00284$ , giving  $k = 0.012$ .

The important point of difference, however, is that whereas McKenzie and Walker's titration experiment showed the displacement of halogen to be complete after 25½ hours, in the present experiments all the halogen was not displaced in this time, but was complete only after some 50 hours, for the initial rate of reaction falls off rapidly as the reaction proceeds, owing to the accumulation of hydrogen ions in the system.

*Reaction between Water and 1-Phenylbromoacetic Acid at 25°.*

The optical kinetic experiment of McKenzie and Walker (*loc. cit.*, p. 1693) was also repeated, but in this case a 4-dcm. tube was used and measurements were made both for the yellow and the green mercury lines. Accordingly 0.3011 g. of *l*-bromo-acid with  $[\alpha]_{589}^{17.7}$  — 177° in benzene was dissolved in 30 c.c. of water (= 1.867N/40) at 25°. Solution occupied 62 minutes, and this is shown as zero-time in Table IV. The values of  $k$  are calculated for a unimolecular reaction.

TABLE IV.

Time.	$\alpha_{3750}^{23^\circ}$ .	$k$ .	$\alpha_{3461}^{25^\circ}$ .	$k$ .
0 mins.	-4.25°		-4.67°	
15	-3.98	0.00427	-4.37	0.00428
30	-3.76	0.00397	-4.09	0.00428
45	-3.56	0.00382	-3.87	0.00404
60	-3.29	0.00414	-3.65	0.00397
90	-2.92	0.00409	-3.21	0.00401
120	-2.64	0.00384	-2.85	0.00396
150	-2.34	0.00384	-2.57	0.00382
180	-2.08	0.00382	-2.27	0.00383
210	-1.83	0.00385	-2.03	0.00378
240	-1.67	0.00373	-1.83	0.00371
270	-1.48	0.00373	-1.63	0.00370
330	-1.20	0.00364	-1.32	0.00361
390	-1.00	0.00350	-1.05	0.00358
450	-0.77	0.00355	-0.85	0.00351
570	-0.53	0.00336	-0.55	0.00340
690	-0.33	0.00332	-0.36	0.00328
25 hrs.	+0.04	0.00275	+0.05	0.00265
30½	+0.07		+0.09	
34½	+0.08		+0.10	
49½	+0.12		+0.14	
120	+0.11		+0.14	

The final change in the rotation of the solution is thus to be attributed to the completion of the displacement reaction, and stages (II) and (III) of McKenzie and Walker's scheme become unnecessary. For comparison, the various results in the two papers previously referred to, calculated on the basis of a uni-molecular reaction, are summarised in the following table, together with the present results.

Experiment.	$k$ (Titration).	$k$ (Optical).
(1) <i>l</i> -Acid, 25° .....	—	0.00373
<i>r</i> -Acid, 25° .....	0.00284	—
(2) <i>l</i> -Acid, 36.8° .....	0.0142	0.0161
(3) Sodium salt of <i>l</i> -acid, 24.8° .....	—	0.0166
"   "   of <i>r</i> -acid, 25° .....	0.0147	—
(4) Sodium salt of <i>l</i> -acid, sodium hydroxide, 24.1° .....	—	0.0179
"   "   of <i>r</i> -acid, sodium hydroxide, 25° .....	0.0181	—
	0.0175	

In cases (1), (2), and (3), the individual values of  $k$  fall off with time, so that the mean values above are calculated over corresponding time intervals. There is a general agreement throughout between the two series of coefficients, but those from the optical measurements are higher than those based on titrations; this difference would agree, as also in the case of the chloro-acid, with a catalytic racemisation of the phenylbromoacetate ion occurring simultaneously with the displacement racemisation. The catalytic racemisation of phenylbromoacetic acid in aqueous acetone solution was clearly demonstrated by McKenzie and Walker (*loc. cit.*, p. 1694). The mechanisms of the conversions of phenylbromoacetic acid and

its sodium salt to mandelic acid and sodium mandelate thus agree with the mechanism above suggested much better than with that advanced previously.

#### *Discussion of Results.*

The above results show that the reaction of water with *l*-phenylchloroacetate and *l*-phenylbromoacetate ions yields simultaneously both *l*-mandelate and *d*-mandelate ions by the same simple reaction from the kinetic point of view, the one reagent thus behaving both "normally" and "abnormally" at the same time in this reaction. The production of phenylaminoacetic acids of either sign from a given phenylchloroacetic acid (Senter and Drew, J., 1915, 105, 638; 1916, 107, 1091) or phenylbromoacetic acid (Senter and Tucker, J., 1918, 113, 140) by reaction with ammonia in various solvents is explicable on the above basis, for the relative values of the velocity coefficients will certainly depend on the solvent medium (compare Senter, Drew, and Martin, J., 1918, 113, 155). In the case of the other conversions similarly studied (Senter, Drew, and Martin, *loc. cit.*; Senter and Ward, J., 1924, 125, 2137; 1925, 127, 1847), it would appear probable that the relative values of the two velocity coefficients differ more widely, agreeing with the production of the same isomeride in excess for all solvents studied.

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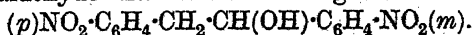
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UNIVERSITY OF LONDON, E.C. 4. [Received, December 19th, 1925.]

## CLII.—*Substituted Cinnamic Amides and Acids.*

By HAROLD AINSWORTH HARRISON and HAROLD WOOD.

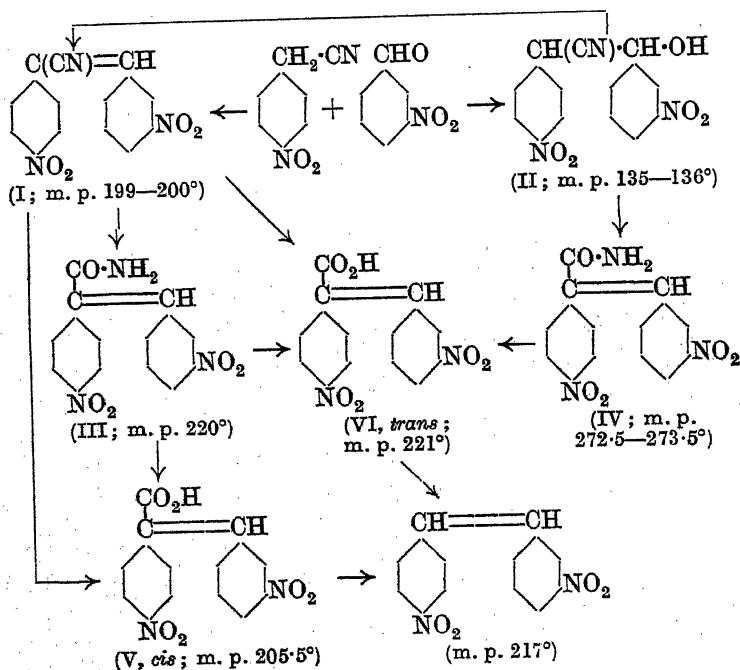
IN a previous paper (this vol., p. 577) the configuration of a 3 : 4'-dinitrochlorostilbene resulting from the elimination of one molecule of hydrogen chloride from the stilbene dichloride was determined by the fact that sulphuric acid converted it into 4-nitrophenyl 3-nitrobenzyl ketone. The constitution of this ketone was deduced from its non-identity with the isomeric 3-nitrophenyl 4-nitrobenzyl ketone obtained by oxidation of the intermediate aldol compound isolated during the condensation of *p*-nitrophenylacetic acid with *m*-nitrobenzaldehyde and therefore having the structure



Another synthesis of 4-nitrophenyl 3-nitrobenzyl ketone [from

3 : 4'-dinitro- $\alpha$ -phenyleinnamamide, utilising Weerman's modification of the Hofmann reaction (*Proc. K. Akad. Wetensch. Amsterdam*, 1907, **10**, 308; *Annalen*, 1913, **401**, 1; *Rec. trav. chim.*, 1917, **37**, 1)], which confirmed the foregoing conclusions, is now described.

When *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde are combined, with sodium ethoxide or piperidine as condensing agent, according to the method of Remse (*Ber.*, 1890, **23**, 3135), 3 : 4'-dinitro- $\alpha$ -phenyleinnamitrile (I) and 3 : 4'-dinitro- $\beta$ -hydroxy- $\alpha$ -phenyldihydrocinnamitrile (II) are formed in about equal quantities. Neither Remse (*loc. cit.*) nor Freund (*Ber.*, 1901, **34**, 3107), both of whom carried out this same experiment, mentions the formation of (II), their sole product being (I).<sup>\*</sup> The aldol compound (II) may be converted into (I) by the action of sulphuric acid, pyridine or piperidine.



Two quite different stereoisomeric *amides* (III and IV) are produced when (I) and (II) are hydrolysed with sulphuric acid. Amide (IV) on further hydrolysis with sulphuric acid yields only one acid (VI), but amide (III) under the same conditions gives a mixture of

<sup>\*</sup> From *o*-nitrobenzaldehyde and *p*-nitrophenylacetonitrile, however, Freund (*loc. cit.*) did isolate two compounds analogous to (I) and (II) above.

(V) and (VI); the same mixture is also formed when the nitrile (I) is directly hydrolysed to the acid stage. When amide (III) is hydrolysed with nitrous acid, however, acid (V) is almost the sole product.

The two acids (V) and (VI) can be separated, by Stoërmer and Prigge's method (*Annalen*, 1915, 409, 20), by taking advantage of their widely differing strengths. Acid (VI) is the weaker, and from analogy with Stoërmer's results (see also Stoërmer and Voht, *ibid.*, 1915, 409, 36) it is provisionally called the "trans" modification; the term applies to the relative positions of the phenyl and carboxyl groups, and not to the two phenyl groups.

Acids (V) and (VI) can both be decarboxylated by heating with piperidine, and yield the same form of 3 : 4'-dinitrostilbene.

#### EXPERIMENTAL.

3 : 4'-Dinitro- $\beta$ -hydroxy- $\alpha$ -phenyldihydrocinnamonnitrile (II).—When the condensation of *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde in presence of piperidine or sodium ethoxide was allowed to proceed for only a few hours the product contained not only 3 : 4'-dinitro- $\alpha$ -phenylcinnamonnitrile (I), m. p. 199—200° after recrystallisation from acetic acid (Remse and Freund give m. p. 195°), but also an equal amount of the intermediate *aldol* (II), which was isolated from the alcoholic mother-liquors, the total yield of the two nitriles being 85—90%. After many recrystallisations from acetic acid the aldol was obtained in yellow, crystalline aggregates, m. p. 135—136° (Found: C, 57.2; H, 3.6.  $C_{15}H_{11}O_5N_3$  requires C, 57.5; H, 3.5%). It is easily soluble in pyridine, nitrobenzene, acetone, or ethyl acetate, less soluble in alcohol or benzene, and somewhat sparingly soluble in chloroform, carbon tetrachloride, or light petroleum. (II) can be converted into (I) by dissolution in cold concentrated sulphuric acid, by dissolving it in hot pyridine and keeping the solution for several days, or by keeping the crude reaction mixture (in presence of alcoholic piperidine) for a week.

The Two Stereoisomeric Forms of 3 : 4'-Dinitro- $\alpha$ -phenylcinnamamide (III and IV).—Each of the nitriles (I) and (II) (20 g.) was carefully dissolved in warm concentrated sulphuric acid (340 c.c.), water (46 c.c.) added, and the mixture heated on the steam-bath for 6 hours. When cold, the solution was poured into 2 litres of water, and the precipitated amide washed with hot dilute ammonia and with water (yield 96—99%). The amide (III), obtained from (I), separated from acetic acid in almost colourless needles, m. p. 220° (Found: C, 57.4; H, 3.6.  $C_{15}H_{11}O_5N_3$  requires C, 57.5; H, 3.5%). It is sparingly soluble in the usual organic solvents, and is not hydrolysed to the acid by boiling with hydrochloric acid for 2 days. The higher-melting form of the amide (IV), obtained from

(II), is even less soluble than (III) in organic solvents. It separates from acetic acid in microscopic prisms and from nitrobenzene in thin plates, m. p. 272.5—273.5° (Found: C, 57.2; H, 3.9%).

*Conversion of the Amide (III) into 4-Nitrophenyl 3-Nitrobenzyl Ketone.*—A paste of the finely powdered amide (20 g.) and boiling methyl alcohol was cooled and added, with shaking, to a solution of sodium hypochlorite during 1 hour. The mixture was then heated at 80° for  $\frac{1}{2}$  hour, much unchanged amide filtered off, the warm liquor acidified with dilute sulphuric acid, and the dark brown precipitate repeatedly crystallised from alcohol (charcoal). The slightly brown needles thus obtained melted at 132°, alone or mixed with 4-nitrophenyl 3-nitrobenzyl ketone. The yield was exceedingly poor, but the constitution of the ketone was proved.

*cis and trans Forms of 3:4'-Dinitro- $\alpha$ -phenylcinnamic Acid (V and VI).*\*—Amide (III) (17 g.) was boiled with a mixture of strong sulphuric acid, acetic acid, and water (125 c.c. of each) for 2 days, the product poured into water, and the filtered solid digested with hot sodium carbonate solution; the addition at 95° of a slight excess of acetic acid precipitated, in 48% yield, the weaker "trans" acid (VI), which crystallised from ethyl acetate in large, pale yellow prisms, m. p. 221° (Found: C, 57.2; H, 3.2; equiv., 316.  $C_{15}H_{10}O_6N_2$  requires C, 57.3; H, 3.2%; equiv., 314). This isomeride is much less soluble than (V) in methyl alcohol or ethyl acetate.

From the hot filtrate after removal of acid (VI), most of the stronger "cis" acid (V) separated out, mixed with a little (VI), and addition of hydrochloric acid to the cold filtrate increased the yield to 36%. After two crystallisations from acetic acid (V) was obtained in rosettes of slightly brown needles, m. p. 205.5° (Found: C, 56.9; H, 3.3%; equiv., 312). It is readily soluble in hot methyl or ethyl alcohol, or acetic acid, and is moderately soluble in cold ethyl acetate.

From the nitrile (I), by hydrolysis under the above conditions, 32% of acid (VI) and 38% of acid (V) were obtained.

Hydrolysis of amide (IV) during 3 days led to the formation of acid (VI) in 77% yield. No acid (V) was discovered, the cold filtrate after removal of (VI) by acetic acid remaining quite clear on addition of hydrochloric acid.

*Hydrolysis of Amide (III) with Nitrous Acid.*—To a solution of amide (III) in cold concentrated sulphuric acid an excess of sodium nitrite was added, with water-cooling. After 2 days, the solution was diluted with water and kept for a week, a little more nitrite being added occasionally. The solid was removed, washed, and

\* For a description of the piperidine salts of these two acids, see this vol.,

thoroughly digested on the filter with hot sodium carbonate solution. Acetic acid was added to the boiling filtrate in slight excess, and the solution again filtered hot to remove a very small amount of precipitate (VI). On cooling, the filtrate deposited acid (V) in 80% yield.

*Decarboxylation of Acids (V) and (VI).*—The acid (3 g.) was dissolved in boiling acetone, piperidine ( $\frac{1}{2}$  c.c.) added, and the acetone distilled off. The intimate mixture thus obtained was heated at 225° for  $\frac{1}{2}$  hour, and, after cooling, the resinous product was washed several times with boiling acetone and finally recrystallised from acetic acid, when it melted at 216°, either alone or mixed with an authentic specimen of 3:4'-dinitrostilbene (for which see this vol., p. 580). The yields from acids (V) and (VI) were respectively 27% and 32%.

In conclusion, one of us (H. W.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant, and the other (H. A. H.) to the Chemical Society Research Fund Committee for a grant for materials. We also thank Professor Lapworth for his continued interest and advice.

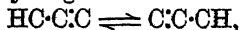
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### CLIII—*The Chemistry of the Glutaconic Acids. Part XIX. A Consequence of Mobility.*

By JOHN PACKER and JOCELYN FIELD THORPE.

THE mobility of the hydrogen atom in the three-carbon system



so far as it has yet been investigated, reaches its maximum in glutaconic acid, causing this substance to exist in only one form, the postulated "normal" form to which has been ascribed the tentative constitution  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CH}(\text{H})\cdot\text{CH}\cdot\text{CO}_2\text{H}$ .

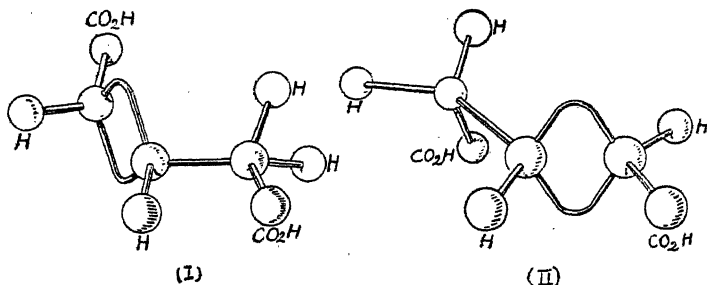
If the corresponding unsaturated formulæ be set up on the models, drawings of which are shown in Fig. 1, it will be found that this mobility may or may not involve a change from the hypothetical *cis*- (I) to the *trans*- (II) form and *vice versa*, depending on the spatial relationship of the methylene hydrogen atoms to the double bond at the time of change.

While this fact is, in itself, no argument for or against the "normal" form, yet it supplies certain explanations and deductions which are of fundamental importance in connexion with the chemistry of these substances.

It is certainly paradoxical that, whilst the two hydrogen atoms

of the methylene group are of equal value owing to the occurrence of free rotation about the single bond, they should have different values when used in bringing about the three-carbon change. But it must be remembered that the positions of the constituent atoms in space are determined by the tendency for like groups to take up positions as remote as possible from one another, a tendency which the molecule can satisfy owing to its power of free rotation about the single bond.

FIG. 1.



In the case of glutaconic acid, where it is immaterial on which side of the central carbon atom the double bond is placed, the tautomeric change would be expected, in the case of the *trans*-form to take place mainly without alteration in stereochemical configuration, and in the case of the *cis*-form to result mainly in conversion into the *trans*-form. In those derivatives of glutaconic acid in which substituting groups are attached to the  $\alpha$ ,  $\beta$ , or  $\gamma$  carbon atom and which may in consequence exist theoretically in more forms, the necessary alterations in the stable positions of the atoms in space may lead to differences in the tendency of the *cis*- and *trans*-forms to be converted into one another by the tautomeric change.

Certain deductions given below render it probable that valuable evidence will be obtainable on these lines regarding the existence or non-existence of the postulated "normal" form. Experiments on this point are now in hand, but it is thought desirable to publish this new point of view at once, because it offers an explanation as to why both forms of, for example, the  $\beta$ -methylglutaconic acids readily yield anhydrides.

The argument has been used by us that the ready formation of the hydroxy-anhydride from both forms of  $\beta$ -methylglutaconic acid favours the assumption of the "normal" form rather than the *cis*- and *trans*-configuration, because in the analogous case of non-mobile systems, for example,  $\alpha\alpha$ -dimethylglutaconic acid,  $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , the *trans*-form gives no anhydride. It is evident, however, from a study of the models, which are similar

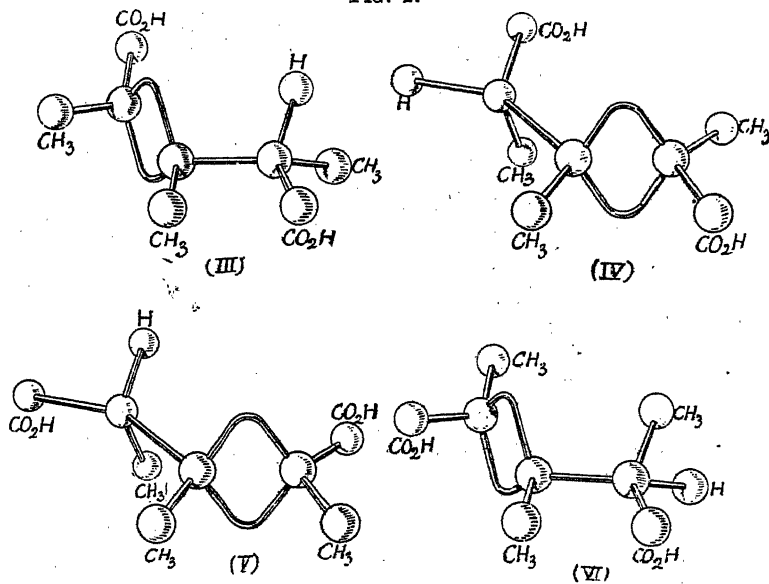


to those for glutaconic acid, that the formation of the hydroxy-anhydride may be preceded by a change of configuration and hence the relative ease of formation of the anhydride from the *trans*- and *cis*-forms is seen to depend on the mobility of the tautomeric system under the conditions of dehydration.

The authors do not wish to call into question the existence of the "normal" form, which is supported by a number of experimental facts, but they desire to point out that :

A. Assuming glutaconic acid to be the stable *trans*-form, it follows that the formation of the hydroxy-anhydride must take

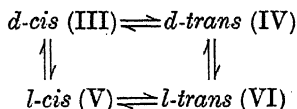
FIG. 2.



place through the *cis*-modification, the inability to isolate the *cis*-form of the acid by hydration of the hydroxy-anhydride being due to the mobility of the system. The existence of two forms of  $\beta$ -methylglutaconic acid, each giving the same hydroxy-anhydride with equal readiness, is due to the same mechanism, but in this case the order of mobility is lower and hence the *cis*-modification can be isolated by hydrating the hydroxy-anhydride under special conditions.

B. In such cases as the  $\alpha\gamma$ -dimethyl- and  $\alpha\beta\gamma$ -trimethyl-glutaconic acids, the theoretically possible *cis*- and *trans*-forms should be capable of resolution into optically active forms, so that, for example, the four forms of the  $\alpha\beta\gamma$ -trimethylglutaconic acids depicted in Fig. 2 should be capable of existence as well as the "normal" form

$\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)\cdot\text{C}(\text{CH}_3)(\text{H})\cdot\text{C}(\text{CH}_3)\cdot\text{CO}_2\text{H}$ . It will be seen that the tautomeric changes may result in the following transformations



but when the tendency of like groups to take up positions as far apart as possible is also considered the following deductions can be made :

(i) The two enantiomorphous *cis*-forms (III) and (V) will tend to pass into the correspondingly active *trans*-forms (IV) and (VI) rather than into each other, unless the change is arrested at the intermediate "normal" form.

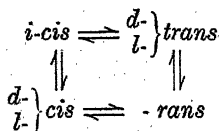
(ii) The two enantiomorphous *trans*-forms (IV) and (VI) will show a greater tendency to interconversion (racemisation) than in the case of the *cis*-forms, and this change may take place to the practical exclusion of transformation into the *cis*-forms.

(iii) If the stable form of the acid is the *trans*-form, it will be capable of resolution into optically active forms which will be distinct from the active forms of the *cis*- (labile) acid ; inability to resolve the stable form would be evidence for the "normal" constitution.

C. In the case of  $\alpha$ - and  $\alpha\beta$ -substituted glutaconic acids the structural isomerides (VII) and (VIII) are theoretically possible, well as the "normal" form

(VII.)  $\text{CO}_2\text{H}\cdot\text{CR}^1\cdot\text{CR}^2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$   $\text{CO}_2\text{H}\cdot\text{CR}^1\text{H}\cdot\text{CR}^2\cdot\text{CH}\cdot\text{CO}_2\text{H}$  (VIII) and each may exist in *cis*- and *trans*-forms. The two forms of (VII) will be incapable of resolution into optically active forms, whilst the two forms of (VIII) will be capable of such resolution under conditions not leading to tautomeric mobility. This should afford an experimental means of determining the position of the double bond in these unsaturated forms.

These isomeric forms are theoretically interconvertible by tautomeric change according to the scheme :



and a study of the models in these cases leads to the following conclusions :

(i) Where  $\text{R}^1$  and  $\text{R}^2$  are positive groups, the *trans*-forms will be more stable than the *cis*-forms.

(ii) Where  $R^2$  is a negative group (e.g.,  $C_6H_5$ ), the relative stability of the *cis*-forms will be increased.

D. The reduction in mobility of the glutaconic system brought about by the substitution of various groups for hydrogen atoms, and the consequent increase in stability of the labile unsaturated forms, can be explained by an application of Thorpe and Ingold's theory of the influence of attached groups on the carbon tetrahedral angle; for the effect of such groups is obviously to reduce the strain in the double bond or two-carbon ring.

The effect of a group in the  $\beta$ -position will be to stabilise both the  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated forms, whilst the effect of a group in the  $\alpha$ -position will be greater in stabilising the  $\alpha\beta$ - than the  $\beta\gamma$ -unsaturated form, so that in general a group in the  $\beta$ -position will have a greater effect in retarding the mobility of the system than will the same group in the  $\alpha$ -position. Hence in the case of  $\alpha$ - and  $\alpha\beta$ -substituted acids, the  $\alpha\beta$ -unsaturated forms (VII) should be more stable than the  $\beta\gamma$ -unsaturated forms (VIII).

In the case of  $\beta$ -phenyl- $\alpha$ -methylglutaconic acid one stable and three labile forms are known. To the *cis*- and *trans*-labile forms of Thorpe and Wood have been assigned the  $\alpha\beta$ -, and to the labile form of Feist the  $\beta\gamma$ -unsaturated structure. If these constitutions are correct, the above considerations favour the "normal" structure for the stable form of the acid, since the only other possible structure is that of the  $\beta\gamma$ -unsaturated *trans*-form, which would be expected to be relatively unstable.

An examination of these acids from the above points of view has been commenced in the hope of thus throwing further light on their constitutions.

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[Received, February 4th, 1926.]

#### CLIV.—*Selective Solvent Action. Part V.* *Salting in.*

By ROBERT WRIGHT.

THE mutual lowering of solubility which takes place when an electrolyte and an organic substance are dissolved together in water has been the subject of many investigations (Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung"), and is the basis of the process of "salting out" when an organic compound is driven out of aqueous solution by the addition of a salt. What may be termed "salting in" is the reverse phenomenon, that is, a mutual increase

in solubility of electrolyte and organic compound when added to the same solvent, which in this case is not pure water but aqueous alcohol.

In former papers (J., 1922, **121**, 2252; 1923, **123**, 2493; 1925, **127**, 2335) it was shown that the addition of a semi-solute to a mixed solvent raised both the vapour pressure and the freezing point of the constituent in which it was insoluble. Thus sodium chloride (or other salt) raised the alcohol vapour pressure of aqueous alcohol, whilst water raised the freezing-point of benzene in an alcohol-benzene mixture. It was pointed out that this might be explained on the solvate hypothesis: in the alcohol-benzene mixture, we have complexes formed between the two constituents; water, when added, competes with the benzene for the alcohol, forming water-alcohol solvates and decomposing some of the alcohol-benzene solvates, thus leaving the solution richer in free benzene and therefore with a higher freezing-point and benzene vapour pressure.

A corresponding effect might be expected in the case of solubility. The addition of salt to aqueous alcohol should form salt hydrates with a consequent increase in the free alcohol present and a corresponding increase in solvent power for benzene or other organic substances. Conversely, the presence of benzene should increase the solvent power of the mixed solvent for a water-soluble solute.

This effect can readily be demonstrated in a qualitative manner. To 100 c.c. of 50% alcohol, benzene is added 1 c.c. at a time until the solution turns turbid; if sodium chloride is now added to the turbid mixture, the liberated alcohol (due to the removal of water for the formation of salt hydrates) will dissolve the excess of benzene and cause the solution to become clear.

Quantitative determinations of this increase of solubility in 50% (by weight) aqueous alcohol have been made with benzene, carbon tetrachloride, and methyl salicylate as alcohol-soluble solutes, and with sodium chloride, sodium nitrate, potassium chloride, potassium bromide, and potassium nitrate as water-soluble salts. It will be noted that none of the salts crystallises with water of crystallisation.

In the method employed, about 12 g. of the aqueous alcohol were weighed in a stoppered tube and excess of salt was added. The benzene, or other organic compound, was weighed in a weight burette and added to the solution in the tube, in small quantities, until turbidity was produced, the quantity of benzene thus added being found by a second weighing. The turbid mixture was shaken in a thermostat at  $20^{\circ} \pm 0.1^{\circ}$  for 6 hours until the solution was saturated with both solutes. About 2 c.c. of the solution were then weighed in a stoppered bottle and the salt was estimated by evaporation to dryness and weighing. Since the proportion of benzene to

aqueous alcohol in the solution is known, the percentage of both salt and benzene dissolved in the aqueous alcohol can be calculated and compared with the percentage when only one solute—benzene or salt—is present. The results obtained are in Tables I and II, and it will be seen that the solubility of each semi-solute is increased by the presence of the other, the increase being considerable in the case of the organic compound.

TABLE I.

Solubilities of organic compounds in 100 g. of 50% aqueous alcohol saturated with different salts at 20°.

Salt present.	None.	NaCl.	NaNO <sub>3</sub> .	KCl.	KNO <sub>3</sub> .	KBr.
Benzene .....	5.8	9.6	9.5	6.7	6.4	7.8
Carbon tetrachloride...	6.4	13.4	8.2	9.9	7.1	9.9
Methyl salicylate .....	6.2	8.2	8.1	7.2	6.9	7.9

TABLE II.

Solubilities of salts in 100 g. of 50% aqueous alcohol saturated with organic compounds at 20°.

Organic compound.	None.	Benzene.	Carbon tetrachloride.	Methyl salicylate.
Sodium chloride .....	9.8	10.6	10.7	10.2
„ nitrate .....	19.4	21.2	20.8	20.4
Potassium chloride .....	6.0	6.5	6.8	6.2
„ nitrate .....	3.7	3.9	3.8	3.8
„ bromide .....	16.4	17.4	17.4	17.3

Four determinations of the solubility of the salt were made in each case, and the results seldom differed by more than one unit in the first decimal place. The solubility of the organic substance was less accurate and, since it was determined by the appearance of turbidity, was always too great, the error being about three units in the decimal place. This error is of less importance in that the increase in solubility of the organic substance is always much greater than that of the salt.

A somewhat more accurate investigation was carried out in the case of benzene and sodium chloride. The solubility of benzene in 50% alcohol was determined at a series of temperatures by adding a weighed quantity of benzene to a definite weight of the solvent and raising the temperature until the turbidity disappeared. A second series was also carried out after 5% of sodium chloride had been added to the aqueous alcohol. The results—which are in Table III—when plotted give two curves practically parallel to each other. The solubility of sodium chloride in 50% alcohol containing small quantities of benzene was also determined, the quantity of benzene being less than that which would produce turbidity. The results are in Table IV.

TABLE III.

Solubility of benzene in 50% aqueous alcohol.		Solubility of benzene in 50% alcohol with 5% NaCl.	
% Benzene.	Temp.	% Benzene.	Temp.
4.57	11.2°	5.80	9.1°
4.78	13.2	6.10	11.8
5.05	15.5	6.39	14.2
5.30	18.0	6.76	16.7
5.61	20.2	7.23	19.2
5.97	22.6	7.57	21.3

TABLE IV.

Solubility at 20° of sodium chloride in 100 g. of 50% aqueous alcohol containing a varying percentage of benzene.

% Benzene .....	0.00	1.91	4.10	5.34	7.95
% Sodium chloride .....	9.80	9.86	9.95	10.10	10.35

As is well known, the addition of potassium carbonate to aqueous alcohol causes the formation of two liquid phases, the greater concentration of the salt being found in the lower (aqueous) layer. The amount of carbonate required to produce turbidity increases with the amount of water present, hence a system which contains just sufficient carbonate to produce turbidity can be cleared by a slight addition of water. This small amount of water can be produced by the desolvation of aqueous alcohol caused by the addition of benzene. For example, if about 0.05 g. of potassium carbonate be dissolved in 2 c.c. of water and 10 c.c. of alcohol be added, a turbid mixture will result, which can be cleared by the addition of either a little water or a larger amount of benzene. A large excess of benzene will again produce turbidity, the benzene forming a layer on top of the aqueous alcohol. Also, if the system contains a larger proportion of carbonate, it is possible, by the addition of benzene, to produce a system of three liquid phases, the benzene and the aqueous salt solution being separated by a layer of aqueous alcohol. That potassium carbonate—like other salts—increases the solubility of benzene in aqueous alcohol is shown by the results given in Table V.

TABLE V.

Solubility at 20° of benzene in 100 g. of aqueous alcohol containing a varying percentage of potassium carbonate.

% Potassium carbonate .....	0.00	1.12	1.67	2.18	2.48	2.68*	2.86
% Benzene .....	5.8	6.4	6.5	7.1	7.3	7.6	8.0

\* Two phases separate.

It is evident from the results shown that with 50% aqueous alcohol there is a mutual increase in solubility of the two types of semi-

solute when they are present together. It has not been considered advisable to attempt to assign any definite degree of solvation to the semi-solutes, as the number of equilibria involved would render any such calculation of very doubtful value.

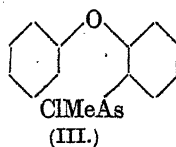
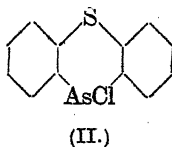
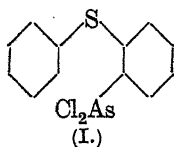
GLASGOW UNIVERSITY.

[Received, March 12th, 1926.]

### CLV.—10-Chlorophenthiarsine, and its Rate of Formation from *o*-Phenylthiolphenyldichloroarsine.

By ELWYN ROBERTS and EUSTACE EBENEZER TURNER.

IN continuation of previous work (Roberts and Turner, J., 1925, 127, 2004), *o*-phenylthiolphenyldichloroarsine (I) has been prepared, and its rate of conversion into 10-chlorophenthiarsine (II) determined. Whereas *o*-phenoxyphenyldichloroarsine undergoes nearly 60% conversion into the ring compound, the sulphur analogue undergoes only about 20% conversion under the same conditions, i.e., when heated at 200° in a current of carbon dioxide.



A further comparison has been made between *o*-phenoxyphenyldichloroarsine and *o*-phenoxyphenylmethylchloroarsine (III) from the same point of view. The chloroarsine is even more stable towards heat than the above phenylthiol compound, undergoing in 6 hours at 200° only about 10% of the possible loss of hydrogen chloride. Moreover, side reactions appear to occur, and it has not been found possible to detect the presence of the expected 10-methylphenoxarsine in the product of decomposition. The latter, when treated with methyl iodide, afforded a little 10-iodophenoxarsine, but no 10 : 10-dimethylphenoxarsonium iodide. This substance has been prepared, for purposes of comparison, by treating with methyl iodide the product of interaction of magnesium methyl iodide and 10-chlorophenoxarsine.

It has been pointed out (Turner and Sheppard, J., 1925, 127, 544) that arsenic trichloride and diphenyl ether do not interact in absence of aluminium chloride. It seemed possible that this might be due to the low boiling point of the mixture, which is well below the temperature at which phenoxyphenyldichloroarsine undergoes conversion into the chlorophenoxarsine. It has, however, been

found that a mixture of phenyldichloroarsine and diphenyl ether boils unchanged at 250–260°, so that the ring closures in question are evidently determined more by collision effects than by those of activation due to increase of temperature.

#### EXPERIMENTAL.

*o*-Nitrodiphenyl Sulphide.—This substance, previously obtained by Mauthner (Ber., 1906, **39**, 3593), is more conveniently prepared by the following method: Potassium hydroxide (61 g.; 1 mol.) was dissolved in 5 c.c. of water, 120 g. (1 mol.) of thiophenol, and then 173 g. (1 mol.) of *o*-chloronitrobenzene and 8 g. of copper bronze were added. The mixture was heated at 170–185° for 2 hours after the initial vigorous reaction had subsided. The cooled product was extracted with carbon tetrachloride, the extract washed successively with alkali and water, and dried over calcium chloride. The solvent was removed, and the residue distilled under diminished pressure. In this manner, 138 g. of *o*-nitrodiphenyl sulphide were obtained, b. p. 210°/15 mm. Crystallisation from light petroleum removed traces of a disulphide, the pure nitro-compound having m. p. 79° (Mauthner gives 77°).

*o*-Aminodiphenyl Sulphide.—The foregoing nitro-compound was reduced with iron, water and ferric chloride (Roberts and Turner, *loc. cit.*). A little thiophenol is formed during the reduction, which proceeds less vigorously than in the case of *o*-nitrodiphenyl ether, but affords not less than an 85% yield of the amine hydrochloride.

*o*-Phenylthiolphenylarsinic Acid.—The pure acid was obtained in 12% yield by the method used for the preparation of phenoxyphenylarsinic acids, and crystallised from alcohol in irregular plates, m. p. 192–194° (Found: As, 24.0.  $C_{12}H_{11}O_3SAs$  requires As, 24.2%). The acid is sparingly soluble in water, and was not converted into the corresponding phenthiarsinic acid when heated with concentrated sulphuric acid, no doubt owing to sulphonation.

*o*-Phenylthiolphenyldichloroarsine.—The preceding arsinic acid, when reduced by the usual process, afforded the crude dichloroarsine as a dark oil, which was purified by conversion into the corresponding oxide (see below), the latter then being reconverted into the dichloroarsine. The latter was thus obtained as a pale yellowish-brown, viscous oil (Found: Cl, 21.3.  $C_{12}H_9Cl_2SAs$  requires Cl, 21.5%). (Traces of the carbon tetrachloride used for the extraction of the pure dichloroarsine were removed by gently heating the substance under diminished pressure for a few minutes.)

*o*-Phenylthiolphenylarsenious oxide separates from benzene in small, white, irregular rhombs, m. p. 187–189° (Found: As, 26.5.  $C_{12}H_9OSAs$  requires As, 27.2%).



*Conversion of o-Phenylthiolphenyldichloroarsine into 10-Chlorophenithiarsine.*—When heated at 200° under the conditions previously described in connexion with the conversion of the phenoxyphenyldichloroarsines into the corresponding chlorophenoxarsines, *o*-phenylthiolphenyldichloroarsine underwent the following course of decomposition :

Time (hours) .....	1	2	3	4	5	6
% decomposition .....	2.2	4.5	7.2	10.2	13.6	17.2

The heating was actually allowed to continue for 24 hours ; the product, almost solid when cold, then readily crystallised from light petroleum (b. p. 80—100°) in sulphur-yellow, rhombohedral masses, apparently consisting of rectangular plates, m. p. 129—130° (Found : Cl, 12.1.  $C_{12}H_8Cl_2SAs$  requires Cl, 12.1%).

*o-Phenoxyphenylmethylchloroarsine.*—*o*-Phenoxyphenyldichloroarsine (19 g.) was dissolved in alcohol containing a little acetone, and a solution of 12 g. of sodium hydroxide in 90 c.c. of water added. The mixture was cooled to 40°, and 8 c.c. of methyl iodide were added slowly. The initial reaction over, the whole was left over-night, when a pale yellow oil separated. The alcohol and acetone were distilled off and the residue was acidified with concentrated hydrochloric acid (25 c.c.); a gummy solid then separated. Potassium iodide (19 g.) was added, and the warmed mixture saturated with sulphur dioxide. The dark red, oily iodoarsine so obtained was converted into the corresponding oxide, and then, by the usual process, into the chloroarsine, which was obtained as a brownish-yellow, viscous oil; it contained a little dichloroarsine (Found : Cl, 13.8.  $C_{13}H_{12}OCl_2As$  requires Cl, 12.1%).

When this substance was heated at 200° in a current of dry carbon dioxide under the same conditions as before, the course of decomposition was as follows :

Time (hours) .....	1	2	3	4	5	6
% decomposition .....	2.5	3.9	5.0	6.4	7.8	9.9

Some methyl chloride was also evolved, and when the decomposition had proceeded for 24 hours, methyl iodide was added to the cooled residue. From the product so obtained, a very small quantity of 10-iodophenoxarsine, m. p. 144°, was isolated (Found : I, 33.8. Calc. : I, 34.3%).

*10:10-Dimethylphenoxarsonium Iodide.*—Finely-powdered 10-chlorophenoxarsine (4 g.) was added gradually to an ethereal solution of magnesium methyl iodide (twice the theoretical amount). It dissolved immediately with evolution of heat; and formation, locally, of a yellow coloration. As soon as it had all been added, the mixture was decomposed by addition of water and then dilute

hydrochloric acid, the ethereal layer separated, washed once with water, dried over sodium sulphate, filtered, and then treated with methyl iodide. After most of the ether had been evaporated, solid separated, which, after crystallisation from alcohol, formed colourless prisms, m. p.  $207^{\circ}$  (with effervescence) (Found: I, 31.1.  $C_{14}H_{14}OIAs$  requires I, 31.7%). The tedious method adopted by Lewis, Lowry, and Bergeim (*J. Amer. Chem. Soc.*, 1921, 43, 890) and by Aeschlimann (*J.*, 1925, 127, 811) does not appear to be necessary in the interaction between Grignard reagents and chlorophenoxarsine.

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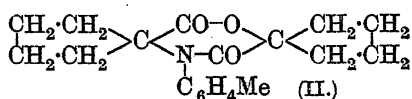
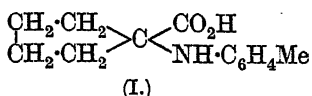
### CLVI.—Some Reactions of 1-*p*-Toluidinocyclopentane-1-carboxylic Acid. A New Carbazole Synthesis.

By STEPHEN HELLICAR OAKESHOTT and SYDNEY GLENN PRESTON  
PLANT.

THE reaction whereby 1-anilinocyclopentane-1-carboxylic acid, on fusion with a mixture of sodium ethoxide and potassium hydroxide, gives carbazole (Plant and Facer, *J.*, 1925, 127, 2037), may follow one of two courses: either the cyclopentane ring may open and form with the carboxyl group the second benzene nucleus of carbazole, or, alternatively, the carbazole may be produced entirely from the anilino-group. It is possible to decide this point by an investigation of 1-*p*-toluidinocyclopentane-1-carboxylic acid (I), which, if the former view is correct, ought to give 3-methylcarbazole as opposed to 3:6-dimethylcarbazole, in accordance with the latter view, on fusion under the same conditions.

We have now condensed *p*-toluidine with cyclopentanone cyanohydrin and have converted the 1-*p*-toluidino-1-cyanocyclopentane so obtained into the corresponding amide, which can be hydrolysed to 1-*p*-toluidinocyclopentane-1-carboxylic acid. On heating this acid with a mixture of sodium ethoxide and potassium hydroxide, 3-methylcarbazole was obtained. Its identity was established by careful comparison of the substance obtained and its picrate with 3-methylcarbazole and 3:6-dimethylcarbazole, which we find can be obtained most conveniently by oxidising the corresponding methyl derivatives of tetrahydrocarbazole with sulphur, and their respective picrates. It seems clear now that the production of carbazole from 1-anilinocyclopentane-1-carboxylic acid involves the enlargement of the carbocyclic system, probably by absorption of

the carboxyl group. A further investigation of this reaction has shown that it proceeds quite as well in the absence of sodium ethoxide and that the sodium or potassium salt of the acid can be used.



1-*p*-Toluidinocyclopentane-1-carboxylic acid is comparatively unstable and loses *p*-toluidine and water on heating above its melting point with the formation of the lactone of 1-1'-hydroxycyclopentane-1'-carboxylyl-*p*-toluidinocyclopentane-1-carboxylic acid (II), showing a behaviour similar to that of 1-anilino-cyclopentane-1-carboxylic acid in this respect.

#### EXPERIMENTAL.

1-*p*-Toluidino-1-cyanocyclopentane.—*cyclopentanone* cyanohydrin will condense with *p*-toluidine when a solution of these substances in benzene is boiled for 12 hours, but conditions similar to those used by Walther and Hübner (*J. pr. Chem.*, 1916, 93, 124) for the preparation of 1-anilino-1-cyanocyclohexane were found to be more convenient. To a solution of *cyclopentanone* (21 g.) and *p*-toluidine (27 g.) in glacial acetic acid (100 c.c.), cooled in ice, potassium cyanide (18 g.), dissolved in a little water, was added. 1-*p*-Toluidino-1-cyanocyclopentane separated in good yield and was washed with water. It crystallised from low-boiling petroleum in colourless needles, m. p. 55° (Found: N, 14.2.  $\text{C}_{13}\text{H}_{16}\text{N}_2$  requires N, 14.0%). The *nitrosoamine*, prepared from an alcoholic solution of the nitrile, dilute hydrochloric acid, and aqueous sodium nitrite, separated from methyl alcohol in yellow prisms, m. p. 58°.

A solution of 1-*p*-toluidino-1-cyanocyclopentane in cold sulphuric acid was kept for 2 days, poured on to ice and the mixture made alkaline with ammonia; the *amide* of 1-*p*-toluidinocyclopentane-1-carboxylic acid was then precipitated. It separated from aqueous methyl alcohol in colourless plates, m. p. 120°. Its *nitrosoamine*, prepared by adding sodium nitrite to the amide dissolved in alcoholic hydrochloric acid, separated from aqueous methyl alcohol in yellow needles, m. p. 132°.

1-*p*-Toluidinocyclopentane-1-carboxylic Acid.—A mixture of the crude amide and concentrated hydrochloric acid was boiled under reflux for 2 hours, evaporated to dryness, the residue treated with an excess of aqueous sodium hydroxide, and the solution boiled and filtered. The addition of glacial acetic acid to the cold filtrate precipitated 1-*p*-toluidinocyclopentane-1-carboxylic acid, which separated from benzene-petroleum in colourless leaves, m. p. 144°

(Found: N, 6.6.  $C_{13}H_{17}O_2N$  requires N, 6.4%). 1-*p*-Toluidinocyclopentane-1-carboxylic acid is soluble in dilute aqueous sodium hydroxide and in dilute hydrochloric acid and gives a *nitrosoamine*, which separates from aqueous methyl alcohol in pale yellow plates, m. p. 114° (decomp.).

On heating 1-*p*-toluidinocyclopentane-1-carboxylic acid in a small distillation flask, water and *p*-toluidine, which was identified by converting it into its acetyl derivative, were evolved. The remainder distilled at a higher temperature, leaving no residue, and, on recrystallisation from petroleum, the *lactone* of 1-1'-hydroxycyclopentane-1'-carboxyl-*p*-toluidinocyclopentane-1-carboxylic acid separated in colourless needles, m. p. 151° (Found: N, 4.7.  $C_{13}H_{23}O_3N$  requires N, 4.5%). This lactone dissolves slowly in cold aqueous sodium hydroxide and is reprecipitated unchanged by the addition of dilute hydrochloric acid. It is not soluble in dilute acids and is unchanged by heating with aniline at 170° or dry ammonia at 200°.

**3-Methylcarbazole.**—An intimate mixture of 1-*p*-toluidinocyclopentane-1-carboxylic acid (16 g.), potassium hydroxide (36 g.), and sodium ethoxide (40 g.) was heated at 350° for 30 minutes. The product was pulverised and added to water, when 3-methylcarbazole separated. It was purified by distillation and subsequent recrystallisation from glacial acetic acid and obtained in colourless, glistening plates, m. p. 207° (compare Ullmann, *Ber.*, 1898, 31, 1697). Its picrate separated from benzene in scarlet needles, m. p. 179° (compare Ullmann, *Annalen*, 1904, 332, 88). The 3-methylcarbazole prepared in this way dissolved in concentrated sulphuric acid to give a pale green solution, which became intensely green on addition of a few drops of nitric acid.

3-Methylcarbazole was also synthesised very conveniently by boiling a solution of 6-methyltetrahydrocarbazole (3 g.; prepared from *p*-tolylhydrazine and cyclohexanone; Borsche, Witte, and Bothe, *Annalen*, 1908, 359, 62) and sulphur (1.05 g.) in pure quinoline (10 c.c.) for 25 minutes and then pouring it into dilute hydrochloric acid-ice. The 3-methylcarbazole which separated, after distillation with a small quantity of iron powder and recrystallisation of the distillate from glacial acetic acid, was obtained in colourless plates, m. p. 207°. Mixed with the product derived from 1-*p*-toluidinocyclopentane-1-carboxylic acid, it showed no depression of m. p., and its colour reactions with concentrated sulphuric acid and nitric acid were as above (compare Ullmann, *loc. cit.*). The picrate of this specimen of 3-methylcarbazole, crystallised from benzene, melted at 180°.

**3:6-Dimethyltetrahydrocarbazole.**—A mixture of 4-methylcyclohexanone (5.5 g.), *p*-tolylhydrazine (6 g.), and alcohol (5 c.c.) was

gently warmed; on cooling, 4-methylcyclohexanone-p-tolylhydrazone separated. It was warmed to boiling with dilute sulphuric acid and heated on the steam-bath for an hour. The 3:6-dimethyltetrahydrocarbazole that separated crystallised from petroleum in small, colourless needles, m. p.  $112^{\circ}$  (Found: N, 7.0.  $C_{14}H_{17}N$  requires N, 7.0%). Its *picrate* separated from benzene in dark red prisms, m. p.  $147^{\circ}$ .

3:6-Dimethylcarbazole was prepared from 3:6-dimethyltetrahydrocarbazole (3.2 g.) and sulphur (1 g.) in quinoline (5 c.c.) as described above. The oily product, which gradually solidified, was distilled with iron powder and thereafter crystallised from benzene, dimethylcarbazole being thus obtained in colourless needles, m. p.  $219^{\circ}$  (compare Täuber and Loewenherz, *Ber.*, 1891, **24**, 1033). 3:6-Dimethylcarbazole gives a faintly brown solution in concentrated sulphuric acid, the colour being intensified on addition of nitric acid. The *picrate* of 3:6-dimethylcarbazole separated from benzene in red needles, m. p.  $192^{\circ}$  (compare Täuber and Loewenherz, *loc. cit.*). A mixture of this 3:6-dimethylcarbazole with the 3-methylcarbazole obtained from 1-p-toluidinocyclopentane-1-carboxylic acid melted completely below  $197^{\circ}$ .

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

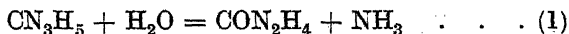
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## CLVII.—*The Hydrolysis of Guanidine.*

By JAMES BELL.

WHILE it is generally accepted that urea is the product of the direct hydrolysis of guanidine in accordance with the simple equation



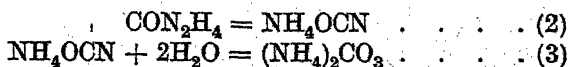
the mechanism of this reaction has not hitherto been investigated. Ossikovszky (*Bull. Soc. chim.*, 1872, **18**, 161) obtained ammonia and carbon dioxide on boiling a solution of guanidine sulphate with excess of alkali and of acid, respectively: he therefore concluded that urea was formed as an intermediate product in this decomposition. The credit of being the first to obtain urea from guanidine is given to Baumann, whose only reference to this reaction consists of one sentence (*Ber.*, 1873, **6**, 1376), where he

states, without giving his experimental evidence, that urea can be obtained by boiling the solution of a guanidine salt with excess of barium hydroxide solution. Almost thirty years later, Fleming (*Chem.-Ztg.*, 1900, 24, 56) obtained impure urea in this way, but gave no quantitative results. Krall, however, in an attempt to investigate the mechanism of this reaction, was unable to obtain any urea on boiling a solution of the free guanidine base under a reflux condenser (*J.*, 1915, 107, 1396).

By means of the xanthhydrol test (Fosse, *Compt. rend.*, 1913, 157, 948) the author has been able to establish definitely the formation of urea, and to determine the extent of the reaction under various conditions. From the results obtained, information has been gained as to the mechanism of the reaction and of the accompanying secondary changes.

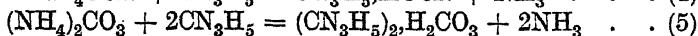
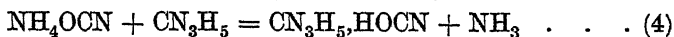
When a solution of free guanidine was boiled under a reflux condenser, ammonia gas was evolved and cyanate, carbonate, and urea were detected in the solution. In certain reactions, where urea, ammonium cyanate, and carbonate are produced, it has been shown that cyanic acid is first formed and is then hydrolysed on the one hand to ammonium carbonate, while on the other it combines in its *iso*-form with ammonia to form urea (Werner and Fearon, *J.*, 1920, 117, 1078). It has now been proved, however, that, in the case of guanidine, urea is the first product formed. When an aqueous solution of guanidine was allowed to remain at the ordinary temperature, the odour of ammonia developed and urea was found present, but no cyanate could be detected by the delicate copper-pyridine test (Werner, *J.*, 1923, 123, 2577). Barium nitrate also gave a negative test for carbonate, which was confirmed by the fact that the alkalinity of the solution remained constant. The first phase in the hydrolysis of guanidine is, therefore, represented by equation 1, the mechanism of which is discussed later.

It would thus appear that the production of ammonium cyanate and carbonate was due to the decomposition of urea, when boiled in the strongly alkaline solution of free guanidine (Werner, *J.*, 1918, 113, 84). This decomposition by guanidine was definitely proved by an experiment in which one equivalent of urea was added to a solution of guanidine, when an increase was obtained in the amount of cyanate and carbonate produced on boiling (Expt. 8). The next phases are therefore:



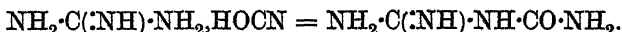
When a sufficiently dilute solution of guanidine was boiled under a reflux condenser, there was no escape of carbon dioxide, resulting

from the dissociation of ammonium carbonate, whereas the amount of ammonia evolved was greater than that required for equation 1. This could only arise from the further changes:



The amount of ammonia evolved was equal, within the limits of experimental error, to that required by these equations. It should be clearly understood that the latter changes (equations 4 and 5) took place under the special conditions stated above. With stronger solutions of guanidine, some carbon dioxide escaped through the reflux condenser and was not, therefore, all fixed as guanidine carbonate. Moreover, when a solution of guanidine was boiled without a reflux condenser, all the carbon dioxide escaped, urea and guanidine cyanate being left in the solution.

When investigating the rates of formation of these different products, it was noticed that, after a time, the proportion of guanidine cyanate present decreased as the reaction proceeded, showing that it also was undergoing change. Bamberger (*Ber.*, 1887, 20, 68) has brought forward evidence for the isomeric change of guanidine cyanate to dicyanodiamidine in accordance with the equation

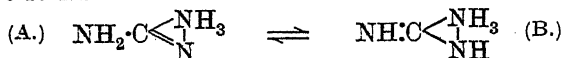


The latter compound, however, could not be detected in the products formed during the hydrolysis of guanidine, and is therefore not formed under the conditions in question. Even after evaporation of some of the neutralised solution to dryness, no change of guanidine cyanate to dicyanodiamidine occurred. There can be no doubt that guanidine cyanate forms only urea or guanidine carbonate, or, in all probability, both these substances, a conclusion which is also the only one consistent with the quantitative data. More definite information as to the hydrolysis of guanidine cyanate would require separate investigation.

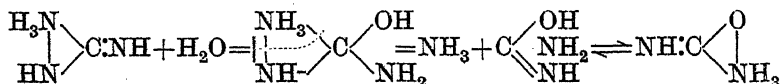
On boiling dilute solutions of guanidine (of approximately  $N/8$  strength), no evidence could be obtained of its dissociation into ammonia and cyanamide. However, when a normal solution was boiled, dissociation to a small extent was indicated by the formation of melamine,  $\text{C}_3\text{N}_6\text{H}_6$ , the tripolymeride of cyanamide. This dissociation is obviously a side reaction and not concerned in the formation of urea, since, in the first place, cyanamide does not produce urea under the conditions of these experiments, and in the second, a greater yield of melamine would have been obtained, in view of the ready polymerisation of cyanamide.

Krall (*loc. cit.*) has given reasons for doubting the usually accepted

formula for guanidine, *viz.*,  $\text{NH}\cdot\text{C}(\text{NH}_2)_2$ , and suggests that in solution, the free base exists probably as an equilibrium mixture of the two forms



Increase of alkali hydroxides would increase the proportion of B, and addition of acids that of A. In the course of the present work, additional evidence has been obtained in favour of this view. When a solution of free guanidine in presence of excess of alkali was kept at the laboratory temperature, the rate of formation of urea was greater than in the case of guanidine alone, whilst the alkali appeared to take no part in the reaction (Expts. 1 and 2). This fact is explained most easily on the above conception of the constitution of guanidine. As a rule, the  $\text{NH}\cdot$  radical is the more readily hydrolysed, and hydrolysis would therefore take place through the B form. The presence of additional alkali increases the proportion of B and therefore increases also the rate of hydrolysis. The mechanism of the reaction may be best explained thus:



This view of the constitution of guanidine has received support from Plimmer in his recent investigation of its behaviour towards nitrous acid (J., 1925, 127, 2658).

#### EXPERIMENTAL.

A solution of free guanidine was prepared by the precipitation of guanidine carbonate solution with one equivalent of barium hydroxide solution and filtering off the barium carbonate. The filtrate, which was an approximately *N*/8-solution, always contained some guanidine carbonate, owing to the absorption of carbon dioxide from the air by the strongly alkaline liquid during filtration. This carbonate was estimated at the outset and the necessary corrections were applied throughout.

In the experiments described, the urea formed was estimated by neutralising an aliquot part of the liquid, evaporating the solution to dryness, extracting the residue with glacial acetic acid, and adding excess of xanthhydrol, dissolved in methyl alcohol. After 12 hours, the precipitate of dioxanthylurea was collected on a weighed filter-paper, washed with alcohol, dried, and weighed. A small correction was applied for the slight solubility of dioxanthylurea in the mixture of acetic acid and methyl alcohol, the value of this



correction being determined in preliminary control experiments. The carbon dioxide in solution was estimated volumetrically, after precipitation as barium carbonate. Cyanates were estimated by precipitation and weighing as silver cyanate.

Dicyanodiamidine was tested for by adding copper sulphate and sodium hydroxide solutions, when the characteristic pink copper derivative of this substance was precipitated. Melamine was identified by its picrate.

In all the experiments, where a solution of guanidine was boiled, the burner was adjusted to secure quiet ebullition only.

*Expt. 1.* Changes produced in  $N/8$ -solution of guanidine at the ordinary temperature.  $a$  is the percentage of guanidine hydrolysed to urea.

Time (days) ...	5	10	20	31	60	70	156	189
$a$ .....	3.25	6.1	11.3	19.2	31.4	35.1	62.4	70.5

No cyanate or carbonate was formed.

*Expt. 2.* Changes produced at the ordinary temperature in  $N/8$ -solution of guanidine containing sodium hydroxide (1 mol.).

Time (days) .....	8	41	102	128
$a$ .....	9.5	34.5	64.9	70.4

Here the velocity of hydrolysis was greater than in the solution of guanidine alone. No cyanate or carbonate could be detected.

*Expt. 3.* Changes produced in  $N/8$ -solution of guanidine after  $1\frac{1}{2}$  hours' boiling under reflux.

100 C.c. of solution were used containing 0.702 g. of the free base. Urea, cyanate, and carbonate in the resulting liquid were estimated. Increase in alkalinity of liquid on boiling = 9.8 c.c. of  $N/10$ -acid (this included the ammonia evolved). This increase could only be due to the formation of ammonium carbonate as in equation 3. Increase in alkalinity, calculated from the carbonate found in solution, = 9.9 c.c. of  $N/10$ -acid. Hence no carbon dioxide escaped through the condenser. The ammonia evolved, calculated from equations 1, 4, and 5, = 8.05 c.c. of  $N$ -acid (Found:  $\text{NH}_3$  = 8.0 c.c. of  $N$ -acid). The following results represent the percentages of the different products, calculated in terms of the guanidine, from which each was originally derived, in accordance with equations 1—5: Urea, 36.5; ammonium cyanate, 9.05; ammonium carbonate, 4.15; guanidine cyanate, 9.07; guanidine carbonate, 8.30. Total, 67.05%.

*Expt. 4.* Changes produced in  $N/8$ -solution of guanidine after boiling under reflux for 3 hours.

Increase in alkalinity, calculated from the carbonate present, = 13.0 c.c. of  $N/10$ -acid. Increase found = 13.0 c.c. of  $N/10$ -acid.

Ammonia evolved = 4.45 c.c. of *N*-acid. Calc.:  $\text{NH}_3 = 11.25$  c.c. of *N*-acid. This was the only experiment in which the ammonia was not all driven out of solution. Found: Urea, 66.0; ammonium cyanate, 6.25; ammonium carbonate, 7.05; guanidine cyanate, 6.25; guanidine carbonate, 14.10. Total, 99.65%.

*Expt. 5.* Changes produced in *N*-solution of guanidine after  $1\frac{1}{2}$  hours' boiling under reflux.

A normal solution of guanidine was prepared by dissolving 4.13 g. of guanidine nitrate in 33.8 c.c. of *N*-sodium hydroxide solution. After boiling, urea, carbonate and cyanate were estimated as before. Increase in alkalinity = 6.4 c.c. of *N*-acid. Increase due to the carbonate found in solution = 3.0 c.c. of *N*-acid. Hence, ammonium carbonate formed = 6.4 c.c. of *N*-acid, and of this, a portion = 3.4 c.c. of *N*-acid, passed through the condenser, whilst the remainder = 3.0 c.c. of *N*-acid, reacted with free guanidine to form guanidine carbonate. Found: Urea, 59.5; ammonium cyanate, 6.45; ammonium carbonate, 9.4; guanidine cyanate, 6.45; guanidine carbonate, 8.9. Total, 90.7%.

Found for the ammonia evolved, 35.2 c.c. of *N*-acid. Calc., 34.2 c.c. The difference is due to ammonia involved in the formation of melamine, a small quantity of which was present. This difference would correspond to a 3% conversion into melamine.

*Expt. 6.* Changes produced in *N*/15-solution of guanidine containing one equivalent of barium hydroxide, after  $1\frac{1}{2}$  hours' boiling under reflux.

The results, in this case, were similar to those of the previous experiments, except that barium cyanate and carbonate were produced instead of the corresponding guanidine salts. The ammonia evolved was not estimated. Found: Urea, 80.0; barium cyanate, 13.4; barium carbonate, 2.9. Total, 96.3%.

*Expt. 7.* Changes produced in *N*/7-solution of guanidine, after 1 hour's boiling without reflux.

The solution was boiled in a distillation flask, connected with a condenser and flask for ammonia absorption. Water was added from a tap funnel at intervals to maintain the volume of the solution constant. No carbonate was found in the solution on boiling. Hence all the carbon dioxide escaped. The amount of ammonium carbonate formed was calculated from the increase in alkalinity.

Found for ammonia evolved, 14.3 c.c. of *N*-acid. Calc., 14.4 c.c. Found: Urea, 73.4; ammonium carbonate, 1.4; ammonium cyanate, 9.6; guanidine cyanate, 9.6%. Total, 94.0%.

*Expt. 8.* Action of guanidine on urea in solution on boiling.

A solution similar to that used in the previous experiment, containing one equivalent of urea (0.9 g.), was boiled for 1 hour under

the same conditions. It was assumed that the changes produced in the guanidine were the same as before. The increase in carbonate and cyanate was therefore due to the decomposition of the added urea. Found: Added urea converted into ammonium cyanate and carbonate = 13.3 and 3.7%, respectively. Therefore total urea decomposed = 17.0%.

From the determination of urea in the two experiments, the decomposition of added urea was calculated to be 21.9%. The difference in these results is due to the fact that, in this experiment, more guanidine was fixed as cyanate than in the previous one, and hence the amount of guanidine hydrolysed would be slightly less.

The author gratefully acknowledges his indebtedness to Professor E. A. Werner, Sc.D., for advice received in the course of this work and to Dr. W. R. Fearon, F.T.C.D., at whose suggestion this investigation was undertaken.

TRINITY COLLEGE, DUBLIN.

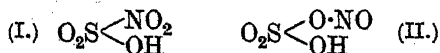
[Received, February 16th, 1926.]

### CLVIII.—Nitrosylsulphuric Acid. Part I.

By GEORGE ALBERT ELLIOTT, LESLIE LEONARD KLEIST, FREDERICK JAMES WILKINS, and HARRY WILLIAM WEBB.

THE object of this investigation was to examine the constitution and properties of nitrosylsulphuric acid.

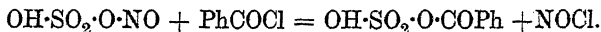
To the substance of the molecular formula  $\text{HSO}_5\text{N}$  have been ascribed two structural formulæ, viz., that of nitrosulphonic acid (I) (Michaelis, *Ber.*, 1874, 7, 1075; Raschig, *Z. angew. Chem.*, 1905, 18, 1032) and that of nitrosylsulphuric acid (II) (Tilden, *J.*, 1874, 27, 630; Lunge, *Ber.*, 1879, 12, 1058). The evidence for the existence of an acid of the structure (I) is unsatisfactory.



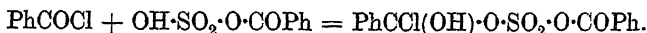
We first prepared the acid by several different methods and found that its melting point and crystalline form did not vary with the method used. Fractional crystallisation from sulphuric acid also failed to effect any change. Therefore, whilst the acid may be tautomeric, the existence of non-dynamic isomerides is improbable.

The action of hydrogen chloride on the crystalline acid at the ordinary temperature rapidly led to the formation of nitrosyl chloride and sulphuric acid, the reaction being reversible, as was

foreshadowed by the work of Tilden (*loc. cit.*). The presence of the nitroso-group thus indicated was more definitely suggested by the reaction between the acid and benzoyl chloride, which produced *dibenzoylsulphuric acid*,  $O_2S(O\cdot CO\cdot C_6H_5)_2$ , whose formation can be satisfactorily explained only on the assumption that nitrosylsulphuric acid contains both a nitroso- and a hydroxyl-group. The mechanism of the reaction would then be as follows. The first stage is the formation of *monobenzoylsulphuric acid* :



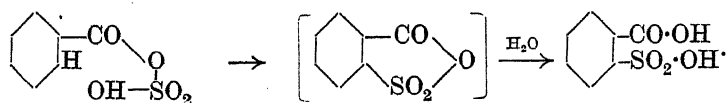
Nitrosyl chloride is actually formed as soon as the two substances are mixed and is rapidly liberated at 35–40° without appreciable heat evolution. The monobenzoylsulphuric acid then reacts additively with a further molecule of benzoyl chloride, probably at the carbonyl group of the latter, and a crystalline product is obtained which loses hydrogen chloride on standing, dibenzoylsulphuric acid being formed :



Confirmation of this mechanism was obtained by examining the reaction between benzoyl chloride and sulphuric acid. Oppenheim (*Ber.*, 1870, 3, 736) states that this reaction yields a benzoylsulphuric acid which rapidly changes to *m*-sulphobenzoic acid on standing, and that the latter is formed exclusively if the reaction is carried out at 150°. No mention of an additive product is made and the experimental data are very meagre. We have found that the substance produced at the ordinary temperature is a crystalline additive compound, to which the constitution  $PhCCl(OH)\cdot O\cdot SO_2\cdot OH$  may most readily be assigned. It loses hydrogen chloride on standing, forming monobenzoylsulphuric acid; this change, however, is inhibited by an atmosphere of hydrogen chloride. The additive compound showed no sign of transformation into sulphobenzoic acid on being kept for 6 months over a dry alkaline absorbent at the ordinary temperature, although during this time the hydrogen chloride was completely eliminated.

At 100°, the highest temperature used in our experiments, conversion of benzoylsulphuric acid into sulphobenzoic acid occurred, but so slowly that the amount formed during our experiments could be neglected in making deductions from the results obtained. The change was a unimolecular one and the product consisted mainly of *o*- and not *m*-sulphobenzoic acid. It is probable that the meta-acid, stated by Oppenheim to be the sole product, is produced by direct sulphonation, and the ortho-acid by intramolecular transformation. The production of the ortho-acid in this way can

be satisfactorily explained by assuming intermediate anhydride formation and subsequent rehydration :

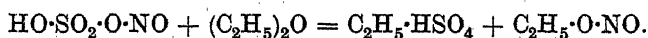


We were unable to obtain pure dibenzoylsulphuric acid by the interaction of benzoyl chloride and sulphuric acid.

The action of acetyl chloride on nitrosylsulphuric acid yielded similar evidence of the presence of the nitroso-group. The first product of the reaction appears to be acetylsulphuric acid, but this changes with great rapidity into the isomeric sulphoacetic acid. The evidence for this change lies in the rapid decrease in the amount of free sulphuric acid produced by the decomposition of the product with water, whilst the total sulphur content of the substance remains constant. The change is very much more rapid than that of benzoylsulphuric acid, but we did not investigate it further as it had already been examined by Van Peski (*Rec. trav. chim.*, 1921, 40, 103) and others.

The action of acetic anhydride on nitrosylsulphuric acid also yielded acetylsulphuric acid. Equimolecular quantities of the two substances without any diluent reacted so violently at the ordinary temperature that the sudden evolution of heat was usually sufficient to shatter the glass container. If the acetic anhydride was in great excess and was kept below 15° during the addition of the nitrosylsulphuric acid, the latter dissolved, and by shaking the solution with silver oxide a substance was obtained to which the constitution  $\text{CH}_3\text{CO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}\cdot\text{CH}_3\cdot\text{CO}_2\text{Ag}$  is assigned.

By the action of ether on nitrosylsulphuric acid, ethyl nitrite and ethyl hydrogen sulphate were produced :



Ethyl hydrogen sulphate and solutions of nitrosylsulphuric acid in sulphuric acid gave no nitroethane, which one would expect to be produced if the acid had the nitrosulphonic structure.

The most important evidence for the nitrosulphonic structure and possible tautomerism of the acid is the work of Biehringer and Borsum (*Ber.*, 1916, 49, 1402). By treating a sulphuric acid solution of dimethylaniline with solid sodium nitrite they obtained mixtures of *p*-nitro- and *p*-nitroso-dimethylaniline. We decided to repeat their work, for three reasons: (1) The setting up of equilibria involving the two forms of nitrous acid and sulphuric acid was not excluded by their method of experiment. (2) Since

they poured a reaction mixture containing an excess of nitrite on ice, direct nitration of unchanged dimethylaniline and secondary oxidation of the nitroso-derivative would be expected. (3) They do not mention the production of sulphur dioxide which would be expected as a by-product from the nitrosulphonic form.

Using a solution of crystalline nitrosylsulphuric acid in sulphuric acid, of concentration equivalent to that used by them, we confirmed the result that both *p*-nitro- and *p*-nitroso-dimethylaniline are produced. We also established the following facts: (1) The percentage yield of the *p*-nitro-derivative increases with the excess of nitrosylsulphuric acid used in the reaction mixture. (2) If an excess of dimethylaniline is used, no oxides of nitrogen are produced by pouring the mixture on ice and no *p*-nitro-derivative is obtained. (3) When an excess of nitrosylsulphuric acid is present and the mixture is poured into absolute alcohol or dry ether, no *p*-nitro-derivative is obtained. Both these solvents rapidly decompose nitrosylsulphuric acid, forming ethyl nitrite and ethyl hydrogen sulphate. (4) When crystalline nitrosylsulphuric acid is added to a solution of dimethylaniline in dilute sulphuric acid (2*N*), in which the former acid is immediately decomposed, both the *p*-nitro- and the *p*-nitroso-derivative are obtained. (5) If a solution of dimethylaniline in concentrated sulphuric acid is added to a dilute solution of nitric acid (10%) or of potassium nitrite (5%), the *p*-nitro-derivative is formed. (6) No sulphur dioxide could be detected in any of the experiments.

All these facts are in accord with the view that the *p*-nitrodimethylaniline is not produced by the action of a presumed nitrosulphonic acid, but is a secondary product obtained by pouring the reaction mixture on ice and is produced either by secondary oxidation of the nitroso-compound or by direct nitration of the dimethylaniline. The results of Biehringer and Borsum do not establish, therefore, in our opinion, the existence of nitrosulphonic acid or the possibility of tautomerism.

#### *Conversion of Nitrosylsulphuric Acid into the Anhydride.*

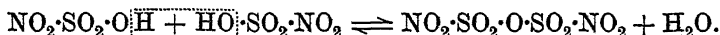
The anhydride of nitrosylsulphuric acid is assumed to have the structure  $\text{ON}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}$  and is stated to be formed by the action of nitric oxide on sulphur trioxide, or of sulphur dioxide on well-cooled nitrogen pentoxide (Berl. *Z. angew. Chem.*, 1910, 23, 2250).

There appears to be no definite experimental evidence for the direct conversion of nitrosylsulphuric acid into the anhydride, a change which would yield important evidence as to structure.

We have examined the change by three methods:

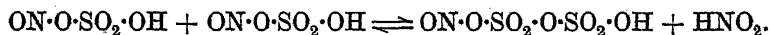
- (1) By the action of heat alone.
- (2) By heating in the presence of dehydrating agents.
- (3) By the determination of the solubility of the acid in sulphuric acid.

*Action of Heat on Nitrosylsulphuric Acid.*—Michaelis and Schumann (*Ber.*, 1874, 7, 1075) carried out a preliminary investigation on this point and suggested that the decomposition took place according to the scheme :



Their experimental methods, however, were very rough, and no experimental evidence was offered that the final product was the anhydride. They ascribe the nitrosulphonic structure to the acid, but it is improbable that an acid of either the nitro- or the nitroso-structure would undergo a decomposition of the type suggested, in view of the great instability of these groups in the molecule.

Theoretically there is another mode of decomposition :



The nitrous acid would then decompose to form nitrogen trioxide and water, which would decompose more nitrosylsulphuric acid. The net result is represented by the equation  $3\text{HSO}_5\text{N} = \text{HS}_2\text{O}_8\text{N} + \text{H}_2\text{SO}_4 + \text{N}_2\text{O}_3$ . When decomposition is complete, the resulting liquid should yield 15.4% of nitrous acid by decomposition with water. If the reaction proceeds according to the suggestion of Michaelis, however, the percentage of nitrous acid so obtained should be 21.8. (By "percentage of nitrous acid" should be understood the amount of nitrous acid obtained by the complete decomposition of the residue with water, calculated as a percentage of the anhydrous substance.)

By following the change in the nitrous acid content we found that the decomposition by heat appears to follow the course suggested by Michaelis.

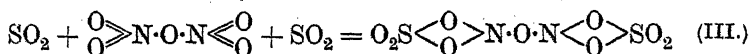
*The Action of Dehydrating Agents.*—The results obtained by heating the acid in the presence of dehydrating agents (phosphorus pentoxide in particular) were unsatisfactory. We were unable to detect the anhydride in the distillate: nitrosylsulphuric acid, the main product obtained, was probably formed by the recombination of sulphur trioxide, water, and nitrogen peroxide in the receiver. Dehydration of nitrosylsulphuric acid was also attempted by making a saturated solution in 98% sulphuric acid at 50°. The solution, after being heated for several hours at 100°, was cooled to 16° and found to be supersaturated. A crystal of nitrosylsulphuric acid induced crystallisation, the product being the un-

changed acid. Further experiments showed that nitrosylsulphuric acid appears to be capable of existence in saturated solution in sulphuric acid even at 300°. This is remarkable in view of the ease with which water is lost on heating the acid alone.

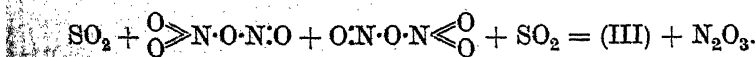
*The Solubility of Nitrosylsulphuric Acid in Sulphuric Acid.*—The method previously described for the attempted isolation of the anhydride would yield positive results only if the anhydride (if formed) were relatively less soluble in sulphuric acid than nitrosylsulphuric acid. We therefore examined the solubility of nitrosylsulphuric acid at 0°, 20.9°, 37.3°, and 49.6° in various concentrations of sulphuric acid. The curves expressing the relationship between the solubility of nitrosylsulphuric acid and the concentration of sulphuric acid all showed a marked increase in the solubility coefficient when the concentration of sulphuric acid reached 73%. Schlesinger and Salathe (*J. Amer. Chem. Soc.*, 1923, 45, 1863) have investigated the absorption spectra of a series of 0.1*N*-solutions of nitrosylsulphuric acid in sulphuric acid of different concentrations. If the concentration of sulphuric acid is plotted against the frequency for a given value of the logarithm of the thickness in their results, the curves so obtained are similar to ours and show a change of slope at a concentration of 78% H<sub>2</sub>SO<sub>4</sub>.

The shape of our curves is not incompatible with the conclusion that anhydride formation takes place.

From some points of view, an alternative structure O<sub>2</sub>S<O>N·OH seems to merit consideration. (1) An acid of this type would lose water on heating to give an anhydride of the structure (III), a change which is parallel to the conversion of nitric acid into nitrogen pentoxide. (2) It offers an explanation of the great difficulty of replacing both the hydroxyl groups of sulphuric acid by the nitroso-group. (3) The structure is in accord with the methods of synthesis of the acid. (4) The behaviour of the acid on reduction is more in accord with this structure than with the nitroso-structure. (5) The synthesis of the anhydride from sulphur dioxide and nitrogen pentoxide (Berl, *loc. cit.*) is readily explicable in terms of the above formula :



and so is the production of the anhydride from nitrogen tetroxide and sulphur dioxide (Provostaye, *Ann. Chim. Phys.*, 1840, 73, 362), in which reaction nitrogen trioxide is a by-product :





It is possible that nitrosylsulphuric acid exists in two tautomeric forms,  $O_2S \begin{smallmatrix} \text{O} \cdot \text{NO} \\ \text{OH} \end{smallmatrix} \rightleftharpoons O_2S \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \text{N} \cdot \text{OH}$ , which are in equilibrium in sulphuric acid solution and in the molten state.

### EXPERIMENTAL.

*Preparation of Nitrosylsulphuric Acid.*—(1) By the addition of dry liquid nitrogen tetroxide to concentrated sulphuric acid at 15–18°. The separation of crystals and the removal of excess of tetroxide were facilitated by blowing dry air through the mass. (2) As above, but using gaseous nitrogen tetroxide. (3) By passing sulphur dioxide, dried by sulphuric acid, into pure nitric acid (94.5%  $HNO_3$ ) at 25°. (4) By leading nitrosyl chloride, generated by heating aqua regia, into concentrated sulphuric acid.

The crystals in each case were rapidly drained by a pump and dried on a porous plate over sulphuric acid. All the products consisted of rhombic prisms (m. p. 73.5°). Tilden (*loc. cit.*) obtained by the last method of preparation a product of m. p. 85–87°, but we have not been able to repeat his work.

*The Action of Benzoyl Chloride.*—A mixture of 1 g.-mol. of nitrosylsulphuric acid with 2.4 g.-mols. of benzoyl chloride was heated for 30 minutes on the water-bath, moisture being excluded. After 12 hours, yellowish-brown, rhombic crystals separated. These were filtered off rapidly on asbestos, washed with dry carbon tetrachloride, and dried on a porous plate over phosphorus pentoxide. The product was very hygroscopic. It had no odour of benzoyl chloride, and on treatment with water it was completely decomposed into sulphuric, benzoic, and hydrochloric acids. Ethyl alcohol was readily converted by it into ethyl benzoate. It was insoluble in all common organic solvents and reacted readily with substances containing a hydroxyl group and with ether and acetone. No evidence of the presence of an acid with a sulphonic group could be obtained. The product was analysed as follows: A weighed sample was warmed with excess of water until completely dissolved. The total acidity was then determined by sodium hydroxide and phenolphthalein, and the sulphuric acid as barium sulphate. Hydrochloric acid was estimated by silver nitrate and ammonium thiocyanate. As an approximate check on the results the benzoic acid was estimated in several samples by removing the sulphuric acid with baryta, slightly acidifying the solution with hydrochloric acid, extracting with ether, and weighing the dried product. The hydrochloric acid content of the samples varied with the time which elapsed before analysis and, in order to make apparent the composition of the acidic residue, the analyses are

expressed in terms of hydrochloric acid-free substance. For convenience of expression also, the acidities obtained after aqueous decomposition are expressed as percentages of the anhydrous substance. The same device is used also for the theoretical values, which are those calculated for  $(\text{PhCO}\cdot\text{O})_2\text{SO}_2\cdot\text{HCl}$ .

Sample.				Calc. for HCl-free product.			Remarks.
	% Total acidity, as $\text{H}_2\text{SO}_4$ .	% $\text{H}_2\text{SO}_4$ .	% HCl.	% Total acidity, as $\text{H}_2\text{SO}_4$ .	% $\text{H}_2\text{SO}_4$ .	% $\text{PhCO}_2\text{H}$ .	
1	71.55	28.66	10.60	64.18	32.06	—	Dried in an atmosphere of HCl.
2	66.00	31.01	3.00	63.89	31.97	—	Analysed after 3 weeks.
3	69.01	29.75	7.30	63.89	32.09	76.73	Analysed after 24 hours.
Theory	71.53	28.61	10.66	64.05	32.02	79.73	

The hydrochloric acid content does not exceed one molecule, and sample 1, dried in hydrochloric acid vapour, approximates closely to the theoretical value. It might be expected that a substance of the nitrosulphonic structure under the conditions of our experiments would yield sulphur dioxide as a decomposition product. 2.4 G.-mols. of benzoyl chloride were heated on the water-bath with 1 g.-mol. of nitrosylsulphuric acid, and the evolved gases drawn through potassium dichromate solution. The amount of sulphur thus found as sulphur dioxide is shown as a percentage of the total sulphur.

Time (hours) .....	2	4	6	8	10	12
% S as $\text{SO}_2$ .....	0.49	0.44	0.26	0.19	0.10	0.02

The results indicate that about 1.5% of the total sulphur is evolved as sulphur dioxide on continued heating at  $100^\circ$ . Although the rate of evolution decreases with time, it is considered that the sulphur dioxide is formed by reduction of sulphuric acid and is not due to the presence of the nitrosulphonic form of the acid, since benzoyl chloride and sulphuric acid yield a similar result (*q.v.*).

*Action of Sulphuric Acid on Benzoyl Chloride.*—The first method used was to mix benzoyl chloride (1 or 2 mols.) with concentrated sulphuric acid. The manner of mixing made a great difference to the purity of the product and to the hydrogen chloride content. If the sulphuric acid was added to the benzoyl chloride, the solution became deep green and most of the chlorine was evolved as hydrogen chloride. If the reverse process was adopted, the coloration was much less and the evolution of hydrogen chloride was very small at the ordinary temperature. Preparations were made in this way,

using sulphuric acid varying in concentration from 96 to 100% at temperatures from 0–40°. The products were treated and analysed as previously described for nitrosylsulphuric acid.

Mode of addition.	Temp.	% Total acidity, as		
		H <sub>2</sub> SO <sub>4</sub> .	% H <sub>2</sub> SO <sub>4</sub> .	% HCl.
2 g.-mol. PhCOCl to 1 g.-mol. H <sub>2</sub> SO <sub>4</sub> .	(1) 30°	76.50	37.55	12.75
	(1A) * 17	67.52	38.29	3.64
	(2) 32	70.11	35.80	10.13
	(3) 30	69.80	36.50	12.91
	(1) 29	77.66	35.65	14.27
1 g.-mol. H <sub>2</sub> SO <sub>4</sub> to 2 g.-mols. PhCOCl.	(2) 30	77.87	35.32	14.47
	(3) † 28	73.30	34.54	9.85
	(4) 0	80.21	38.27	15.30
	(5) 0	79.41	37.43	15.16
	(6) 0	80.63	38.77	14.70
1 g.-mol. H <sub>2</sub> SO <sub>4</sub> to 1 g.-mol. PhCOCl.	(1) 0	77.30	43.90	8.19
	(2) 0	76.40	45.08	7.01
Theory for PhCO·O·SO <sub>2</sub> ·OH, HCl		82.18	41.09	15.34

\* After 48 hours over lime.

† After keeping 48 hours.

The last two preparations, when calculated to hydrochloric acid-free product, gave total acidity = 72.24, 72.06% H<sub>2</sub>SO<sub>4</sub>, and sulphuric acid = 47.82, 48.48%, respectively, whereas the values theoretically required are 72.77 and 48.51%.

The repetition of the exact experimental conditions used in the case of nitrosylsulphuric acid yielded products which appeared to be mixtures of mono- and di-benzoylsulphuric acids or of the mono-acid and sulphobenzoic acid. Preparations carried out at 16° and 30° gave similar products. At 0°, however, the products were very near in composition to the mono-acid.

In view of the difficulty of purifying the products, the method of preparation was further improved by dissolving the benzoyl chloride in excess of dry carbon tetrachloride, adding the 98% sulphuric acid gradually with continuous shaking, and keeping the mixture for 30 minutes, with exclusion of moisture. In this way, it is immaterial whether 1, 2, or 3 molecular proportions of benzoyl chloride are used and the temperature can also be varied between 0–35° without affecting the purity of the product: the yield is theoretical. Analyses of typical products were as follows:

	% Total acidity as H <sub>2</sub> SO <sub>4</sub> .	% H <sub>2</sub> SO <sub>4</sub> .	% HCl.
1	78.40	44.02	9.20
2	78.88	43.64	10.00
3	78.78	43.31	10.04

The total sulphur content of the products was determined by fusion, and the fact that the figure so obtained was identical with that for the percentage of sulphuric acid obtained by decomposing the substance with water was taken to indicate the absence of

sulphobenzoic acid from the products. This estimation was carried out as follows. To 1 g. of the substance contained in a platinum dish about 5 g. of moistened sodium peroxide were added and the mixture was stirred with a platinum rod. The product was intimately mixed with 30—40 g. of a mixture of 1 part of potassium nitrate and 2 parts of fusion mixture. The top of the mass was then covered with 15—20 g. of fusion mixture, and the whole heated gently until fusion was complete. If signs of charring appeared, the determination was repeated. The method was much quicker than a Carius estimation and better than the Eshka method for the substances under analysis. The method is given in detail, as duplicates showed it to be quite satisfactory.

*Transformation of Benzoylsulphuric Acid into Sulphobenzoic Acid.*—Determinations were made of the total sulphur content of a number of products by fusion, and of the sulphuric acid produced by decomposition with water. The samples were prepared using equimolecular proportions of sulphuric acid and benzoyl chloride at 0°, 16°, and 120°. The results were as follows :

	1.	2.	3.
Sulphuric acid by water treatment ( $\text{H}_2\text{SO}_4$ %)	42.31	43.30	37.40
Total sulphur (by fusion) as $\text{H}_2\text{SO}_4$ % .....	42.16	43.16	37.43

This evidence for the absence of sulphobenzoic acid is conclusive unless the latter is completely decomposed by treatment with warm water. No satisfactory information could be found in the literature on this point and therefore we determined the velocity of transformation of benzoylsulphuric acid into sulphobenzoic acid at 100°, the highest temperature used in our experiments. 70 G. of monobenzoylsulphuric acid were heated, in a constant-temperature bath at 100°, in a flask fitted with a moisture trap. The gases were drawn off continuously through potassium dichromate and the sulphur dioxide content was estimated. Samples of the residue in the flask were drawn off at intervals and the sulphuric acid produced by decomposition with water was estimated. At the conclusion of the heating the total sulphur content of the residue was determined by the fusion method previously described.

Time (hours).	% $\text{H}_2\text{SO}_4$ obtained.	k.	% Total S lost as $\text{SO}_2$ .
0	43.20	—	—
10	36.67	0.01639	0.26
15	33.83	0.01630	0.25
20	31.14	0.01637	0.23
25	28.75	0.01628	0.22

Total sulphur content of the residue after 25 hours = 42.10% as  $\text{H}_2\text{SO}_4$ .  $k$  is calculated on the basis of a unimolecular reaction.

*Isolation of Sulphobenzoic Acid* [With R. PEPPERELL].—The above

material which had been heated for 25 hours at  $100^{\circ}$  was warmed with 500 c.c. of water and concentrated to 250 c.c. The precipitated benzoic acid was filtered off and the sulphuric acid precipitated with baryta and filtered off. This filtrate was concentrated to 100 c.c., and the excess of barium exactly precipitated with sulphuric acid. The barium sulphate and any further benzoic acid were removed and the filtrate was evaporated to small bulk and extracted with ether until no further benzoic acid could be obtained. The residue on final concentration on the water-bath solidified to an amorphous hygroscopic mass which was dried by heating to  $105^{\circ}$  (Found: S, 16.1. Theory for  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ : S, 15.8%). The substance did not melt sharply, but was completely molten at  $135^{\circ}$ . The anhydride (m. p.  $129\text{--}130^{\circ}$ ) was prepared by refluxing with acetyl chloride for 2 hours and extraction with benzene. The acid also condensed readily with resorcinol in presence of zinc chloride to give a phthalein. The product was hence *o*-sulphobenzoic acid, but the original substance contained some meta-acid also.

*Action of Acetyl Chloride.*—25 G. of nitrosylsulphuric acid were added slowly to 35 g. of acetyl chloride dissolved in 100 c.c. of carbon tetrachloride, and the mixture was warmed to  $30\text{--}35^{\circ}$  to start the reaction. A vigorous evolution of nitrosyl chloride occurred, the temperature rising to  $60\text{--}70^{\circ}$ , and a yellow, viscous, non-crystallisable oil separated. This was washed repeatedly with carbon tetrachloride and ligroin and analysed as rapidly as possible by methods similar to those used in the case of the corresponding benzoyl derivative (Total acidity, as  $\text{H}_2\text{SO}_4$ , 101.9;  $\text{H}_2\text{SO}_4$ , 68.4.  $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_3\text{H}$  requires 105.0 and 70.0%, respectively). The substance was completely decomposed by water into acetic and sulphuric acids.

The product was heated under reflux in carbon tetrachloride for 30 minutes and the percentage of sulphuric acid obtained by decomposition with water was reduced to 54.32% from 68.40%. After another hour's refluxing, it was further reduced to 27.58%, the total sulphur content remaining constant.

*Action of Acetic Anhydride.*—(1) 10 G. of acetic anhydride were dissolved in 200 c.c. of carbon tetrachloride and 12 g. of nitrosylsulphuric acid were added. On refluxing for 30 minutes a yellow oil separated, from which the last traces of solvent were removed in a vacuum. (2) 5 G. of nitrosylsulphuric acid were dissolved in 200 c.c. of acetic anhydride, the mixture being kept cool, and the solution was shaken with 5 g. of dry silver oxide. The silver oxide was rapidly converted into a gelatinous suspension, which was filtered off in a vacuum, washed with acetic anhydride, and dried over sulphuric acid. The product was amorphous and

hygroscopic and on treatment with water gave no oxides of nitrogen. The resulting solution gave no precipitate with barium nitrate. Liebermann's reaction showed the presence of nitrite or a nitroso-group in the substance. The salt contained sulphur, nitrogen, and silver, in addition to carbon, hydrogen, and oxygen (Ag, by heating, 31.5; by conversion to  $\text{AgCl}$ , 32.0. S, estimated as  $\text{BaSO}_4$ , 9.4.  $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO}$ ,  $\text{CH}_3\cdot\text{CO}_2\text{Ag}$  requires Ag, 32.1; S, 9.5%).

*Action of Nitrosylsulphuric Acid on Dimethylaniline.*—(1) To a solution of 35 g. of dimethylaniline in 40 c.c. of concentrated sulphuric acid a solution of 70 g. of nitrosylsulphuric acid in 30 c.c. of sulphuric acid was added, at 10–15°. By following the experimental procedure of Biehringer and Borsum (*loc. cit.*) there were obtained: *p*-nitrodimehtylaniline, 63%; *p*-nitrosodimehtylaniline, 37%. (2) The above experiment was repeated using half the amount of nitrosylsulphuric acid (*i.e.*, an excess of dimethylaniline). No nitro-derivative was obtained but only the nitroso-derivative. (3) Quantities as in Expt. (1) were used and the mixture was dropped slowly into absolute alcohol at 0°. No nitro-derivative was obtained. By pouring the product into 300 c.c. of dry ether a mixture of the sulphates of dimethylaniline and *p*-nitrosodimehtylaniline was obtained. Some nitric oxide was evolved on first mixing the reactants, but no sulphur dioxide could be detected at any stage of the reaction.

*Action of Heat on Nitrosylsulphuric Acid.*—(1) 30 G. of the crystalline acid were heated for 30 minutes at 350° in a wide glass tube fitted with a moisture trap; nitrogen trioxide was rapidly evolved during the first 15 minutes. A pale yellow, very viscous oil remained (Found:  $\text{HNO}_2$ , 19.3%).

(2) 50 G. of nitrosylsulphuric acid were heated under similar conditions at 300° for 9 hours. The residual oil was analysed as before (Found:  $\text{HNO}_2$ , 20.2%).

At both these temperatures sulphur trioxide was evolved owing to the decomposition of the product, and this fact may explain the poor agreement with the value required by the suggestion of Michaelis. On attempting to carry out the decomposition at temperatures low enough to ensure that no sulphur trioxide was produced, it was found that the rate of decomposition was so slow that several weeks would be required for complete decomposition.

(3) 50 G. of the acid were heated in a constant-temperature bath at 150°. Samples were withdrawn at intervals and analysed as before.

Time (hrs.)	...	0	0.75	11.3	16.5	26.3	39.0	46.8	59.3	137.0
% $\text{HNO}_2$	.....	35.9	32.8	30.7	30.2	29.7	29.0	28.1	27.5	25.8

(Theoretical value for anhydride, 21.8%  $\text{HNO}_2$ .)

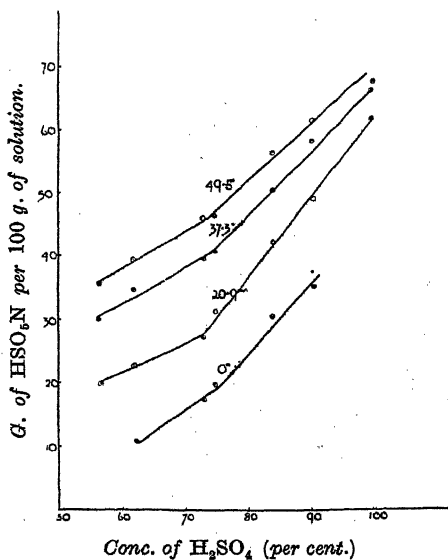
Similar determinations were carried out at 115° and 130° and in each case the early rapid evolution of nitrogen trioxide was observed. The slowness of decomposition of nitrosylsulphuric acid at the lower temperatures is undoubtedly due to the stabilising influence of sulphuric acid, which is a secondary product of the reaction. The decomposition of the acid begins at 73°, when it begins to melt.

The general conclusion to be drawn from the results is that the mode of decomposition suggested by Michaelis is in accord with the experimental facts. It must be pointed out, however, that (1) sulphuric acid is produced by the decomposition and tends to prevent further loss of nitrogen trioxide on heating, and (2) water escapes from the reaction zone in the early part of the heating; consequently the nitrous acid content of the residue would be expected to exceed the theoretical value.

*Solubility of Nitrosylsulphuric Acid in Sulphuric Acid.*—The general method of solubility determinations was adopted, the nitrosylsulphuric acid in excess being agitated with sulphuric acid of known concentration contained in thin glass tubes in a thermostat. Each tube was protected against the ingress of moisture by running the stirrer through a glass tube sealed with petroleum jelly. The sulphuric acid used was of concentrations 56.7, 62.1, 73.1, 74.9, 84.1, 90.4, and 99.8%.

After 3 hours, a sample was filtered through glass wool into a weighing bottle containing sulphuric acid and, after weighing, the contents were made up to 100 c.c. with sulphuric acid, the nitrous acid then being estimated by a method specially devised for this work. At the higher temperatures and with the lower concentrations of sulphuric acid, some of the solutions contained free nitrous acid (*i.e.*, not combined as nitrosylsulphuric acid). In order to determine the amount of the latter acid actually present, this

FIG. 1.



free nitrous acid was removed by rapid blowing with air followed by immersion in the thermostat for 15 minutes. The sample was then taken in the usual way. The results here given are also shown graphically in the figure.

Conc. of $\text{H}_2\text{SO}_4$ (%).	56.7	62.1	73.1	74.9	84.1	90.4	99.8	Temp.
Solubility of nitrosyl-	—	11.9	17.3	19.7	30.5	35.1	—	0.0°
sulphuric acid as per	19.3	22.6	27.0	31.4	42.4	49.2	62.0	20.9
100 g. of solution.	29.9	34.3	39.4	40.8	50.2	58.5	66.1	37.3
	35.6	39.3	46.0	46.2	56.5	61.6	67.8	49.6

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### CLIX.—*Unsymmetrically Substituted Dinitro- and Diamino-derivatives in the Stilbene and Tolane Series. Part II. The Mode of Addition of Water to 3:4'-Dinitro- and Diamino-tolanes.*

By HAROLD AINSWORTH HARRISON.

IN a former communication (this vol., p. 577) it was shown that two nitro-groups unsymmetrically situated in the two benzene nuclei of stilbene exert a definite influence on the reactivity of chlorine atoms attached to the carbon atoms in the side chain. The experiments now described indicate that similar influences are discernible in the unsymmetrically substituted dinitro- and diamino-tolanes, as exemplified by the mode of addition of the elements of water to the triple bond. Polarity considerations again appear to furnish a guide in determining the seat of reactivity.

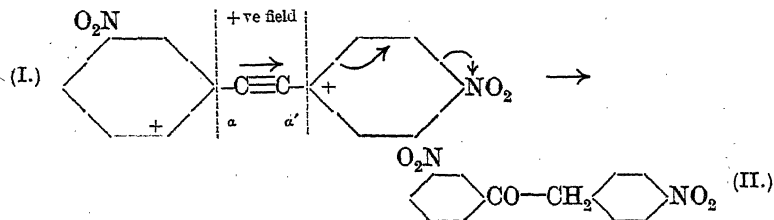
3:4'-Dinitrotolane (I) was obtained from the dichloride or dibromide of 3:4'-dinitrostilbene, or from  $\alpha$ -chloro-4:3'-dinitrostilbene, by the action of alcoholic potassium hydroxide. In the preparation from the dibromide, although traces of the stilbene were undoubtedly produced by loss of bromine (compare Pfeiffer and Kramer, *Ber.*, 1913, 46, 3655), no difficulty was experienced in obtaining the pure tolane.

3:4'-Dinitrotolane assumed the elements of water only with great reluctance.\* With the nitro-groups in these positions it was to be expected from the alternating polarity rule that harmonious combination of directing influences would exist, tending to make such a configuration exceedingly reactive and prone to attack at

\* All the ortho-substituted nitrotolanes prepared by Reinhardt (*Ber.*, 1913, 46, 3598), by Pfeiffer and Kramer (*ibid.*, 1913, 46, 3655), and by Pfeiffer (*Annalen*, 1916, 411, 72) take up the elements of water with remarkable ease. It is significant, however, that neither Reinhardt nor Pfeiffer mentions the addition of water to 4:4'-dinitrotolane.



the carbon atoms in the side chain. But no such enhanced reactivity was manifested and the yield of 3-nitrophenyl 4-nitrobenzyl ketone (II) was small. Robinson, Allan, Oxford, and Smith (this vol., p. 401) recognise the existence of two quite distinct effects when a nitro-group is attached to the benzene ring: the one arising from the conjugation of the nitroxyl with the nucleus and resulting in positive charges on the ortho- and para-carbon atoms, and the other a general electrical effect over the nucleus and the side chain. Applying these conceptions to 3:4'-dinitrotolane, one deduces respectively that a smaller density of electrons exists in the region of the two carbon atoms marked + than in the region of their immediate neighbours, and that the acetylenic carbon atoms  $\alpha\alpha'$  are under the influence of a strong positive field, which inhibits reactivity towards positive ions at both centres. Since, however, the positive charge in the *p*-nitrophenyl group is nearer the acetylenic bond than is that in the *m*-nitrophenyl group, the electrons of the acetylenic bond will be displaced in the direction of the arrow, that is, from  $\alpha \rightarrow \alpha'$ .<sup>\*</sup> Addition of water, therefore, though difficult, takes place as follows:



It is also possible that the *p*-nitrophenylacetylene group is a conjugated system, but the existence of such conjugation could only be disclosed by experiments with anionoid reagents.

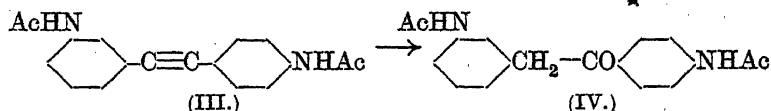
An attempt to investigate the influence of the amino-groups on the elimination of hydrogen chloride from 3:4'-diaminostilbene dichloride was unsuccessful, owing to the impossibility of retaining the chlorine atoms in the molecule during the reduction; 3:4'-*di*-aminostilbene was the sole product.<sup>†</sup>

3:4'-*Diaminotolane*, like the nitrotolane, was very reluctant to assume the elements of water; this inertness is at first sight the more surprising in view of the peculiar ease with which 4:4'-diaminotolane passes into the deoxybenzoin, warm dilute hydrochloric acid

<sup>\*</sup> Similar cases have been considered by Lucas and his colleagues (*J. Amer. Chem. Soc.*, 1924, **46**, 2475; 1925, **47**, 1459, 1462).

<sup>†</sup> Replacement of the chlorine atoms by hydrogen does not occur, since 3:4'-*di*-aminodibenzyl (prepared for purposes of comparison) coincided with none of the products obtained during the whole investigation.

effecting its quantitative conversion (Reinhardt, *Ber.*, 1913, 46, 3598). Under no conditions\* did sulphuric acid bring about the corresponding reaction in the case of 3:4'-diaminotolane; during one reduction experiment only, in which zinc and hydrochloric acid were employed, was a small amount of 4-aminophenyl 3-aminobenzyl ketone produced. From the *diacetyl* derivative of the aminotolane (III), however, the action of concentrated sulphuric acid resulted in the formation of the *diacetyl* derivative of this ketone (IV) in good yield, its constitution being inferred from its non-identity with 3-acetylaminophenyl 4-acetylaminobenzyl ketone, prepared from the corresponding nitrophenyl nitrobenzyl ketone (this vol., p. 579).



The conception of combined general and alternating polar effects again proves valuable here. Electronic repulsion from the two acetyl-amino-groups, resulting from their conjugation with the respective benzene nuclei, produces a strongly negative field in the region of the acetylenic carbon atoms, which are consequently in a highly reactive state. Addition of water thus takes place with great ease.

The mechanism of reaction of the free aminotolane, on the other hand, is obscured by salt formation, but to account for the great difference in reactivity between 4:4'- and 4:3'-diaminotolane it is only necessary to suppose that the former exists in hydrochloric acid as its mono-acid salt, and the latter as its di-acid salt. In fact, the author ventures to suggest that the diquaternary ammonium base derived from 4:4'-diaminotolane would assume the elements of water with great difficulty.

#### EXPERIMENTAL.

**3:4'-Dinitrostilbene Dibromide.**—Finely-divided 3:4'-dinitrostilbene (21.6 g.) (this vol., p. 580) was suspended in chloroform (1 litre), bromine (12 c.c.) added, and the whole kept during 2—4 days. The stilbene gradually dissolved and later the dibromide partly crystallised. The solvent and excess of bromine were then distilled off, and the solid residue† was recrystallised from boiling glacial acetic acid (about 925 c.c.). The yield was 90%. As with the dichloride, two forms could be obtained by fractional crystallisation. The pure  $\alpha$ -form is sparingly soluble in acetic acid,

\* The concentration and temperature were varied over a wide range.

† This, unlike the dichloride (this vol., p. 581), did not char during removal of the last few c.c. of solvent.

crystallising in almost white, thick prisms, m. p.  $234^{\circ}$  (Found: Br, 36.9.  $C_{14}H_{10}O_4N_2Br_2$  requires Br, 37.2%). Its production seems to be favoured by longer exposure of the chloroform solution to daylight. The pure  $\beta$ -form is more soluble in acetic acid or chloroform, crystallising from the former solvent in pale brown, minute plates, m. p.  $214^{\circ}$  (Found: Br, 36.95%). Both forms are sparingly soluble in most organic solvents; they separate from boiling nitrobenzene in small prisms. Even the  $\beta$ -form, which in substances of this type usually reacts differently from the  $\alpha$ -form (compare Pfeiffer, *Ber.*, 1912, 45, 1810), on being heated with pyridine at  $90^{\circ}$  for 2 hours loses both bromine atoms, reverting to the stilbene.\*

3:4'-Dinitrotolane (I).—The mixture of dibromides (22.8 g.) was suspended in boiling alcohol (220 c.c.), and a solution of potassium hydroxide (6.6 g.) in water (15 c.c.) added. After being boiled under reflux for 1 hour, the mixture was allowed to cool to  $50^{\circ}$  and the brown solid filtered off. After being well washed with cold alcohol and then with water, the product was crystallised twice from glacial acetic acid, and then from a large volume of alcohol to free it from traces of stilbene (see p. 1232). The pure tolane melted at  $173$ – $174^{\circ}$ ; the yield was 70% (Found: C, 62.3; H, 3.2.  $C_{14}H_8O_4N_2$  requires C, 62.7; H, 3.0%). It is easily soluble in hot benzene, nitrobenzene, acetone, or ethyl acetate, less readily in acetic acid or chloroform, somewhat sparingly soluble in ethyl alcohol, and very sparingly soluble in carbon tetrachloride, carbon disulphide, ether, or light petroleum. It produces a deep red solution in strong sulphuric acid.†

*Addition of water.* The nitrotolane (1 g.), obtained in a fine state of division by pouring an alcoholic solution into water, was dissolved in cold concentrated sulphuric acid. After being maintained at  $15^{\circ}$  for 30 minutes,‡ the solution was slowly poured on to ice, and the slightly resinous deposit filtered off and dissolved in acetone. Slow evaporation of the solvent left behind dark glistening plates, which after three crystallisations from alcohol (charcoal) melted at  $101^{\circ}$ , alone or mixed with an authentic specimen of 3-nitrophenyl 4-nitrobenzyl ketone (this vol., p. 582). Although the yield was only fair, no other product was isolated.

\* Unlike the dibromide of the parent substance (Limpricht, *Annalen*, 1868, 145, 338), 3:4'-dinitrostilbene dibromide does not yield the corresponding benzil when heated with water under pressure, even at  $215^{\circ}$  for 60 hours.

† Compare the bluish-violet colour given under similar conditions by 2:4-dinitrotolane (Pfeiffer, *loc. cit.*).

‡ Any other conditions, such as alteration of temperature, use of solvents, change in concentration or duration, resulted in a charred product or recovery of the unchanged nitrotolane.

**3 : 4'-Diaminostilbene.**—A solution of the dinitrostilbene (2 g.) in boiling acetic acid (15 c.c.) was cooled to 70° and zinc dust (10 g.) and hydrochloric acid (40 c.c.) were gradually added with stirring; the reaction was complete in  $\frac{3}{4}$  hour. The boiling solution was filtered, and, on cooling, the *hydrochloride* separated in yellow, pearly plates or needles.\* The free amine after recrystallisation from alcohol formed small, yellow plates or needles, m. p. 156° (Found : C, 80.0; H, 6.9.  $C_{14}H_{14}N_2$  requires C, 80.0; H, 6.7%). It is very soluble in ethyl acetate or acetone, less readily in alcohol, ether or benzene, and sparingly soluble in chloroform, carbon tetrachloride, carbon disulphide or light petroleum. The *diacetyl* derivative crystallises from methyl alcohol in clumps of needles, m. p. 226—227° (Found : C, 73.3; H, 6.3.  $C_{18}H_{18}O_2N_2$  requires C, 73.5; H, 6.1%). This derivative is very soluble in ethyl acetate, soluble in acetone or alcohol, and sparingly soluble in benzene or chloroform. It gives no colour with cold concentrated sulphuric acid.

**3 : 4'-Diaminodibenzyl.**—The diaminostilbene (1.2 g.) was reduced with sodium (2 g.) in boiling ethyl alcohol (30 c.c.), the reaction being complete in  $\frac{1}{2}$  hour. When cold, the opaque solution was acidified with dilute hydrochloric acid and a small amount of tar removed by extraction with ether. The free base crystallised from the warm solution on addition of dilute sodium hydroxide (weight of crude product = 0.95 g.), and when recrystallised from aqueous alcohol formed small, white plates, m. p. 73—75°. It is easily soluble in acetone, alcohol, ether or benzene; the *hydrochloride* is readily soluble in water, from which it crystallises in needles. The *diacetyl* derivative crystallises from aqueous alcohol in small clusters of thick needles, m. p. 177° (Found : C, 72.7; H, 6.9.  $C_{18}H_{20}O_2N_2$  requires C, 73.0; H, 6.8%). It is readily soluble in alcohol, acetone, or ethyl acetate, moderately easily soluble in hot chloroform, and almost insoluble in benzene. It gives no colour with cold sulphuric acid.

**Reduction of 3 : 4'-Dinitrostilbene Dichloride.**—3 : 4'-Diaminostilbene was also obtained, though with difficulty, from 3 : 4'-dinitrostilbene dichloride by reduction in alcoholic solution with zinc and hydrochloric acid at 15°.† The reduction was incomplete, and the light brown *substance* which remained after filtration of the normal reaction product, when crystallised from alcohol melted

\* It is essential to isolate this amine as its hydrochloride, otherwise the melting point varies over a range of 50°.

† No reduction took place with iron powder and calcium chloride, whilst stannous chloride and acetic acid yielded a mixture of products exceedingly difficult to purify.

at 202—205° (Found: C, 65.2; H, 3.0%). It contained chlorine, but gave an immediate intense purple colour with cold concentrated sulphuric acid, and was therefore not the unchanged dichloride (see this vol., p. 582). On the other hand, it could not be diazotised. Its constitution was not further investigated.

*Reduction of  $\alpha$ -Chloro-4:3'-dinitrostilbene.*—Facile reduction occurred when crystalline stannous chloride (25 g.) in 80% acetic acid (25 c.c.) was added to the chlorostilbene (5 g.) dissolved in boiling glacial acetic acid (50 c.c.). The solution was almost neutralised with sodium hydroxide,\* and the tin precipitated by hydrogen sulphide. The filtrate was boiled and neutralised, and the free ketonic base recrystallised several times from alcohol (charcoal); after purification, it formed rosettes of almost colourless needles, m. p. 153°, which were not identical with 3:4'-diaminostilbene, m. p. 156°, obtained from the dichloride (see above), since an intimate mixture melted about 15° below this temperature.

A better yield of the diacetyl derivative of this base was obtained by shaking the crude reduction liquor, while still warm, with acetic anhydride in presence of sodium acetate. After standing over-night, the solution was poured into water and the suspended solid extracted with methyl ethyl ketone. The ketone layer, which separated after the addition of a large quantity of calcium chloride, was dried over potassium carbonate, the solvent removed, and the diacetyl compound recrystallised three times from methyl alcohol with the addition of ether; it then melted at 204°. (The properties of these two compounds are described below.)

*3:4'-Diaminotolane.*—The nitrotolane (3 g.) was boiled with alcohol (25 c.c.), and the suspension quickly cooled to 10°. Zinc dust (5 g.) was added, and then, very slowly, hydrochloric acid (17 c.c.) † during 1 hour, the temperature being maintained at 10—15°. The solution of the hydrochloride was filtered from much (2 g.) unreduced nitrotolane and the precipitated amine was extracted with ether and recrystallised from aqueous alcohol, when it formed light brown needles, m. p. 124—125° (Found: C, 80.6; H, 6.1.  $C_{14}H_{12}N_2$  requires C, 80.8; H, 5.8%). It dissolves easily in alcohol, ether, ethyl acetate or acetone, rather less readily in hot benzene or chloroform, and is sparingly soluble in carbon disulphide or light petroleum. It is not converted into the deoxybenzoin by boiling with hydrochloric acid. Its *diacetyl* derivative crystallises from methyl alcohol in thick needles, m. p. 226° (Found: C, 73.8;

\* The free amine appears to be somewhat unstable to hydrogen sulphide in presence of alkali; possibly a sulphur atom is incorporated in the molecule (compare Jones and Robinson, J., 1917, **111**, 911).

† Zinc and acetic acid give coloured by-products.

H, 5.55.  $C_{18}H_{16}O_2N_2$  requires C, 74.0; H, 5.5%). This diacetyl derivative, unlike those of diaminostilbene (m. p. 226—227°) and diaminodibenzyl (m. p. 177°), gives an immediate red colour with cold concentrated sulphuric acid.

**4-Acetylaminophenyl 3-Acetylaminobenzyl Ketone (IV).**—Pure 3:4'-diacetyldiaminotolane (III) (0.3 g.) was dissolved in cold concentrated sulphuric acid (3.0 c.c.), and the temperature maintained at 15° for  $\frac{1}{2}$  hour. No hydrolysis took place under these conditions. The deep red solution was then poured on to ice, and the mauve-coloured solid at once filtered off. It slowly changed to a grey non-crystalline mass, which by purification from alcohol was transformed into almost white needles, m. p. 204° (Found: C, 69.3; H, 6.1.  $C_{18}H_{18}O_2N_2$  requires C, 69.7; H, 5.8%). The yield was good, and no other product was detected. This diacetyl compound was identical with that obtained from the reduction of  $\alpha$ -chloro-4:3'-dinitrostilbene (see above). It is soluble in alcohol, dilute acetic acid, or ethyl acetate, but sparingly soluble in ether. It no longer gives a red colour with cold concentrated sulphuric acid.

**4-Aminophenyl 3-Aminobenzyl Ketone.**—During the course of one experiment on the reduction of 3:4'-dinitrotolane with zinc and hydrochloric acid at 70—80°, after separation of the hydrochloride of the normal reduction product, precipitation of the mother-liquors with alkali yielded a brown solid which, after being twice crystallised from aqueous alcohol, melted at 156°. Its melting point was depressed 20° by admixture of an authentic specimen of 3:4'-diaminostilbene (m. p. 156°),\* but not at all by addition of the amine (m. p. 153°) formed on reduction of  $\alpha$ -chloro-4:3'-dinitrostilbene; its diacetyl derivative, m. p. 204°, was identical with that obtained by the action of sulphuric acid on 3:4'-diacetyldiaminotolane. Without doubt it was a deoxybenzoin produced by addition of water to the triple bond of the tolane, probably under the influence of the metal, since boiling hydrochloric acid alone effected no change (Found: C, 74.0; H, 6.4.  $C_{14}H_{14}ON_2$  requires C, 74.3; H, 6.2%). This amine is soluble in all the usual organic solvents, and crystallises in clusters of slightly brown, flat needles from alcohol.

**3-Acetylaminophenyl 4-acetylaminobenzyl ketone** was obtained when the corresponding dinitro-ketone (1.3 g.) was reduced at 10° with zinc and hydrochloric acid, as in previous experiments. The crude amine isolated from the hydrochloride was at once acetylated, and the product recrystallised from alcohol, when it melted at 184—186° (Found: C, 69.35; H, 6.0.  $C_{18}H_{18}O_2N_2$  requires C, 69.7; H, 5.8%). The solubilities of this diacetyl derivative were similar to those of

\* Which even under these conditions, therefore, is not produced (compare Reinhardt, *loc. cit.*).

the isomeric ketone, m. p.  $204^{\circ}$ , but a mixture of the two melted at  $170$ — $179^{\circ}$ . This dissimilarity definitely establishes the constitution of 4-acetylaminophenyl 3-acetylaminobenzyl ketone, and consequently the mode of addition of water to 3 : 4'-diaminotolane and to its diacetyl derivative.

In conclusion, the author wishes to thank Professor Lapworth for suggesting the research, and the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the expenses.

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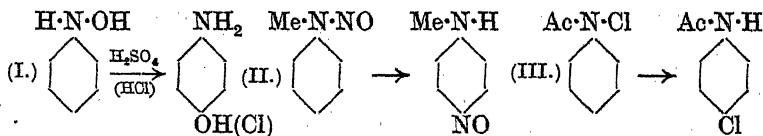
[Received, January 4th, 1926.]

## CLX.—*Investigations in the Diphenyl Series. Part I.* *Migration Reactions.*

By FRANK BELL, JOSEPH KENYON, and PERCY HARRY ROBINSON.

In view of the appearance of a paper by Vorländer (*Ber.*, 1925, 58, 1913), in which 4-hydroxylaminodiphenyl is described, and of another by Scarborough and Waters on the chlorination and bromination of 4-aminodiphenyl (this vol., p. 557), it has been thought advisable to communicate some of the results already obtained by the authors in the same field.

The literature shows that numerous attempts have been made to elucidate the spatial relations of the two nuclei in diphenyl compounds, and there is considerable evidence in favour of the view of the closeness of the 4, 4'-positions in some derivatives. If the 4, 4'-positions in diphenyl are close together, there is a reasonable probability that those types of reactions which involve the para-migration of certain groups in simple benzene compounds might also be exhibited, under appropriate conditions, by certain derivatives of diphenyl, the migrating group passing from position 4 to position 4'. Migration reactions in the diphenyl series analogous to the following have been looked for, but have not been found :

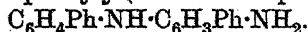


In the corresponding diphenyl compounds decomposition occurs in case (II), whilst in cases (I) and (III) migration does take place, not, however, to the 4'-position but most probably to the adjacent 3-position.

There is an extensive literature on the preparation of diphenyl by the thermal decomposition of benzene, the most recent account being that of Lowe and James (*J. Amer. Chem. Soc.*, 1923, **45**, 2666), who, however, used an apparatus which is outside the resources of an ordinary laboratory. A simpler device is described in the experimental part; chlorobenzene, under similar treatment in the apparatus described, underwent extensive carbonisation, and no 4:4'-dichlorodiphenyl was obtained. The nitration of diphenyl was carried out by a modification of the methods due to Hübner (*Annalen*, 1881, **209**, 339) and Van Hove (*Bull. Soc. chim. Belg.*, 1923, **32**, 52).

By the reduction of 4-nitrodiphenyl with aluminium amalgam and moist ether, there is obtained a complex mixture of 4-azodiphenyl, 4-azoxydiphenyl, 4-aminodiphenyl, and 4-hydroxylaminodiphenyl, together with unchanged nitrodiphenyl. By crystallisation of this mixture from benzene, a 30% yield of 4-hydroxylaminodiphenyl is obtained. Vorländer (*loc. cit.*), who gives no experimental details whatever, states that the compound was prepared "nach bekanntem Verfahren" and melted at 132—134°.

The insolubility of 4-hydroxylaminodiphenyl militates seriously against migration experiments under favourable conditions. Sulphuric acid of various concentrations was employed at first, but as the minimum concentration of this acid necessary for solution of the hydroxylamino-compound at the ordinary temperature is above 50%, deep-seated decomposition occurs, and no crystalline material other than 4-azoxydiphenyl can be isolated from the products of the reaction. By the action of 10% sulphuric acid at 100°, a very small proportion of a new compound was formed. This substance has not yet been thoroughly investigated, but it is believed to be 4-diphenyl(4-amino-3-diphenyl)amine,



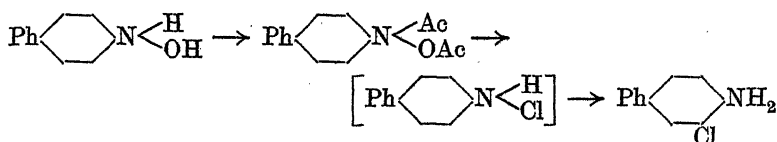
When hydrogen chloride is passed into a dry ethereal solution of 4-hydroxylaminodiphenyl, or when this compound is left for some time in contact with strong hydrochloric acid, 4-hydroxylaminodiphenyl hydrochloride is formed, which, on heating, decomposes to give principally 4-azoxydiphenyl.

An alcoholic solution of hydrogen chloride converts 4-hydroxylaminodiphenyl almost completely into 4-azoxydiphenyl, but at the same time there is produced a very small proportion of a compound which melts at 69° and contains chlorine.

Acetyl chloride reacts readily with 4-hydroxylaminodiphenyl to yield a diacetyl derivative believed to be diacetyl-4-hydroxylaminodiphenyl. This compound can be prepared in almost theoretical yield by dissolving 4-hydroxylaminodiphenyl in warm acetic



anhydride, and when warmed with strong hydrochloric acid it undergoes hydrolysis and simultaneous conversion into a chloro-base (m. p. 69°), the hydrochloride of which hydrolyses very readily, and in consequence has not been prepared in a sufficiently pure state for analysis. The chloro-base yields a monoacetyl derivative of m. p. 146° which is identical with that obtained by the action of acetic acid on diphenyl-4-acetylchloroamine (*vide* below), so that the course of this reaction is probably expressed by the following scheme :



4-Methylaminodiphenyl was prepared by treating 4-acetylaminodiphenyl with sodium and methyl iodide with subsequent elimination of the acetyl group, and was purified by conversion into its nitroso-derivative.

4-Nitrosomethylaminodiphenyl, both alone and when suspended in ether (in which it is only sparingly soluble), was mixed with an alcoholic solution of hydrogen chloride, when slow reaction ensued with evolution of gas. No nitroso-4-methylaminodiphenyl was found in the reaction mixture, which consisted mainly of 4-methylaminodiphenyl together with a little of the unchanged substance.

4-Diazomethylaminodiphenyl is a by-product in the preparation of 4-nitrosomethylaminodiphenyl from the crude secondary amine, which probably contains a little 4-aminodiphenyl.

Diphenyl-4-acetylchloroamine. It is clear from the literature that the preparation of aryl acyl chloroamines is susceptible to slight variations in experimental conditions (compare Armstrong, J., 1900, 77, 1047; Chattaway and Orton, J., 1901, 79, 275).

A similar susceptibility has been found in the case of 4-acetylaminodiphenyl, which, however, reacts rapidly and quantitatively at 70—80°. One sample yielded 67% of diphenyl-4-acetylchloroamine after only 10 minutes' heating. Further, the state of subdivision is very important, and may account for the difficulties met with by Armstrong and his students in the case of acetanilide (*loc. cit.*). When the 4-acetylaminodiphenyl was powdered mechanically, the yields were poor.

When diphenyl-4-acetylchloroamine is warmed with glacial acetic acid it is transformed into a chloro-4-acetylaminodiphenyl believed to be 3-chloro-4-acetylaminodiphenyl (compare above).

No trace of 4'-chloro-4-acetylaminodiphenyl was detected, although its presence was specially sought.

3-Chloro-4-acetylaminodiphenyl results directly if the sodium hypochlorite solution used is above normal in strength.

A quantitative yield of 3-chloro-4-acetylaminodiphenyl results also from the direct chlorination of 4-acetylaminodiphenyl in acetic acid. Again no trace of 4'-chloro-4-acetylaminodiphenyl was detected. This is in marked contrast with the bromination of 4-acetylaminodiphenyl in acetic acid, which yields 30% of the theoretical quantity of 4'-bromo-4-acetylaminodiphenyl together with 65% of a bromo-base (m. p. 65°) not yet fully examined.

#### EXPERIMENTAL.

*Diphenyl.*—The heating coil, which consists of about 1 yard of 32 gauge nichrome wire, is loosely threaded through a strip of mica 5"  $\times$  1 $\frac{1}{4}$ " and suspended in the neck and body of a 5-litre flask fitted with an upright condenser. Benzene (1 $\frac{1}{2}$  litres) is placed in the flask and boiled. When benzene is dripping freely from the condenser, the current is switched on, and by means of a sliding resistance is gradually raised to the value (about 3 amps.) at which the flask begins to fill with fumes. Little attention is required, and at the end of about 30 hours the liquid is transferred to a flask and distilled. Benzene comes over first, and then the temperature rises rapidly. The fraction b. p. 245–260° is collected and crystallised from alcohol. The yield of pure diphenyl averages 9 g. per hour.

*Nitration of Diphenyl.*—To a solution of diphenyl in acetic acid (2 parts) at 70–90°, nitric acid (*d* 1.51; 2 $\frac{1}{2}$ –3 mols.) is added in small quantities. The solution darkens, and when about one-third of the acid has been added a visible and steady reaction sets in. The remaining acid is added more carefully, the experiment taking 1 $\frac{1}{2}$  to 1 $\frac{1}{2}$  hours from the first addition of acid. After cooling, the crystalline crop of 4-nitrodiphenyl is filtered off, and the filtrate diluted with water. The oily layer thus precipitated is separated roughly from the aqueous layer and filtered from a further amount of 4-nitrodiphenyl. The oil is heated in a current of steam to free it from residual acid and unchanged diphenyl, and then distilled in a vacuum. Moisture and a trace of diphenyl come over first, and the main bulk distils at 188–193°/20 mm. The distillate is dissolved in alcohol at 40° and the crystals of 4-nitrodiphenyl which separate on cooling are filtered off. After evaporation of the alcohol, 2-nitrodiphenyl crystallises in characteristic large plates or prisms. 100 G. of diphenyl give 60–70 g. of 4-nitrodiphenyl, m. p. 114°, and 35–39 g. of 2-nitrodiphenyl, m. p. 35–37°.

*4-Hydroxylaminodiphenyl.*—A solution of 4-nitrodiphenyl (50 g.) in ether (1300 c.c., previously distilled from sodium hydroxide) is cooled in a freezing mixture and to it is added aluminium amalgam (10 g.), in very thin sheets, at such a rate that the reaction does not become too vigorous; the reaction vessel is shaken from time to time. Very little hydrogen is evolved if the mixture is kept cold, and the amalgam takes about 2 hours for complete reaction. The mixture is then filtered, the bulky aluminium hydroxide washed several times with dry ether, and the filtrate and washings are evaporated to dryness. The residue is dissolved in the minimum amount (about 250 c.c.) of boiling benzene, and the yellow solution allowed to cool. 4-Hydroxylaminodiphenyl separates in almost colourless, glistening leaflets which appear to fill the whole bulk of the liquid. These are filtered off and dried (yield, 10–14 g.). The compound melts at 152–154° to a red liquid which sets, and in turn melts at 188–190° (Found: C, 77·8; H, 6·0; N, 7·7.  $C_{12}H_{11}ON$  requires C, 77·8; H, 5·9; N, 7·6%).

The formation of a deep damson colour with concentrated sulphuric acid is a sensitive reaction for this compound.

4-Hydroxylaminodiphenyl (2 g.) was maintained in the molten state for 30 minutes, and the cooled residue (1·86 g.) dissolved in boiling benzene. The solution on cooling deposited crystals of 4-azodiphenyl, and after evaporation of the benzene, the residue consisted of a mixture of 4-azoxydiphenyl (m. p. 211–212°) and 4-aminodiphenyl (m. p. 52°).

On treatment of an ethereal solution of 4-hydroxylaminodiphenyl with hydrogen chloride or by leaving a suspension in concentrated hydrochloric acid for some time, the *hydrochloride* is obtained as a white powder (Found: HCl, 16·6.  $C_{12}H_{11}ON, HCl$  requires HCl, 16·5%). The principal product obtained on heating the hydrochloride is 4-azoxydiphenyl.

*Action of 10% sulphuric acid.* 4-Hydroxylaminodiphenyl (5 g.) is triturated with sulphuric acid (600 c.c. of 10%), and the mixture heated on a steam-bath until the whole assumes a deep chocolate colour. It is then filtered hot, and the insoluble residue extracted with 2 litres of boiling water. The filtrates deposit amine sulphates, which are filtered off and suspended in sodium carbonate solution. The mixture is boiled and, after addition of some alcohol, filtered from a trace of impurity. On cooling, the liquid fills with fine, silky crystals, which are filtered off and crystallised from aqueous alcohol; m. p. 156°. It is difficult to make certain that the product is quite free from 4-aminodiphenyl, since the sulphate of this compound must be present in the filtrate. As the compound is insoluble in sodium hydroxide, it is tentatively suggested that it

may be produced by the *o*-semidine change of an intermediate reactive 4-hydrazodiphenyl (Found : C, 85.0; H, 6.1.  $C_{24}H_{20}N_2$  requires C, 85.6; H, 6.0%).

By the action of an alcoholic solution of hydrogen chloride on the hydroxylamine there was obtained a small quantity of a chloro-base, m. p. 69° (see below).

*Diacetyl-4-hydroxylaminodiphenyl* was prepared by dissolving 4-hydroxylaminodiphenyl in acetic anhydride and pouring the solution, filtered from a little 4-azoxydiphenyl, into excess of water. The well-washed precipitate crystallised from alcohol in clusters of short, thick needles, m. p. 119° (Found : C, 71.2; H, 5.8; N, 5.2.  $C_{16}H_{15}O_3N$  requires C, 71.4; H, 5.6; N, 5.2%).

This compound gives a deep damson colour with concentrated sulphuric acid. This diacetyl derivative (24 g.) was dissolved in 90 c.c. of concentrated hydrochloric acid by warming on a water-bath, 500 c.c. of water were added, and the whole was filtered while boiling. The hydrochloride which separated on cooling was difficult to purify by crystallisation, as it was so readily hydrolysed. It was decomposed by sodium carbonate, and the oil obtained was filtered off after solidification. By repeated crystallisation from aqueous alcohol, it was obtained as a constant-melting chloro-base, m. p. 69° (Found : N, 6.9.  $C_{12}H_{10}NCl$  requires N, 6.9%).

It gives an acetyl derivative which crystallises from alcohol in glistening needles, m. p. 146° (Found : C, 68.4; H, 5.0; N, 6.0.  $C_{14}H_{12}ONCl$  requires C, 68.4; H, 4.9; N, 5.7%).

*4-Aminodiphenyl*.—This compound is formed during the preparation of 4-hydroxylaminodiphenyl, but its separation from the accompanying azoxy-, azo-, and nitro-compounds is difficult. The benzene filtrate from 4-hydroxylaminodiphenyl was therefore evaporated to dryness, the residue finely powdered and suspended in ether, aluminium amalgam added until the ethereal solution became colourless, the filtered solution evaporated to dryness, and the residue dissolved in boiling alcohol; on cooling, 4-hydrazodiphenyl separated in colourless, glistening needles, m. p. 167—169°. This was filtered off, and by dilution of the mother-liquor 4-aminodiphenyl (m. p. 52—53°) was obtained.

4-Nitrodiphenyl is converted directly into 4-aminodiphenyl by the same process when excess of aluminium amalgam is added. This appears to be the cleanest method of preparation, and the yield is good.

*4-Hydrazodiphenyl* was heated with hydrochloric acid and sulphuric acid of various strengths, but only 4-azodiphenyl and 4-amino-diphenyl could be isolated from the products, thus confirming the observation of Rassow (*J. pr. Chem.*, 1901, 63, 449).

4-Azoxydiphenyl was isolated from the product obtained by partial reduction of 4-nitrodiphenyl, by means of its ready solubility in benzene and insolubility in alcohol. It melts at  $212^{\circ}$  whether prepared by this method or by Zimmermann's (*Ber.*, 1880, 13, 1960), who, however, gives the m. p. as  $206^{\circ}$  (Found: C, 81.8; H, 5.2; N, 8.1. Calc.: C, 82.3; H, 5.1; N, 8.0%).

4-Azodiphenyl (m. p.  $249^{\circ}$ ) was obtained by distilling a mixture of 4-azoxydiphenyl and iron filings under reduced pressure.

4-Methylaminodiphenyl.—A mixture of 4-acetylaminodiphenyl (31.5 g.; m. p.  $171^{\circ}$ ), dry xylene (200 c.c.), and sodium (5 g.) was heated at  $130^{\circ}$  for 2–3 hours and cooled, methyl iodide (25 g.) was added, and the reaction completed by warming for a short period. The xylene was distilled off and the residue heated under reflux with alcoholic potash for 15 hours. Alcohol and xylene were removed in a current of steam, and the residue was extracted with ether. The ethereal extract was dried with sodium sulphate and after evaporation of the ether the residue distilled almost wholly at  $198$ – $202^{\circ}/20$  mm., the distillate setting to a semi-solid mass. This was best purified by conversion into the nitroso-derivative, and subsequent decomposition of this by boiling with concentrated hydrochloric acid according to the following procedure. The semi-solid mass was dissolved in glacial acetic acid, and the calculated amount of sodium nitrite added. The precipitate was filtered off, dried on porous plate, and boiled with alcohol, which extracted the nitrosoamine from an insoluble yellow product (A). On cooling the filtrate, the nitrosoamine crystallised, and was obtained as an almost colourless, microcrystalline powder, m. p.  $116^{\circ}$ , by recrystallisation from alcohol (Found: C, 73.6; H, 5.7.  $C_{13}H_{12}ON_2$  requires C, 73.6; H, 5.7%).

The nitrosoamine gave brilliant colours at the various stages of the Liebermann reaction. To obtain the secondary base, the nitroso-compound was boiled with concentrated hydrochloric acid. The hydrochloride thus obtained crystallised from dilute hydrochloric acid as a white powder (Found: HCl, 16.6.  $C_{13}H_{13}N.HCl$  requires HCl, 16.6%). On decomposition with sodium carbonate, 4-methylaminodiphenyl was obtained as an oil which rapidly solidified and had m. p.  $38^{\circ}$ . It was readily soluble in almost all organic solvents, gave an acetyl derivative, m. p.  $118$ – $119^{\circ}$ , which was very soluble in alcohol and separated from aqueous alcohol in a gelatinous condition.

This base is much better characterised as its *p*-toluenesulphonyl derivative, which was readily prepared by the action of *p*-toluenesulphonyl chloride in pyridine solution, and crystallised from alcohol in lustrous, white needles, m. p.  $128^{\circ}$  (Found: N, 4.2.  $C_{20}H_{19}O_2NS$  requires N, 4.2%).

Its constitution is easily checked, since it may also be prepared by shaking the *p*-toluenesulphonate of 4-aminodiphenyl with methyl sulphate and sodium hydroxide. The *p*-toluenesulphonate of 4-aminodiphenyl, prepared by the usual method, crystallises from alcohol in colourless needles, m. p. 160° (Found: N, 4.5.  $C_{19}H_{17}O_2NS$  requires N, 4.3%).

The yellow product (A) obtained in the preparation of 4-nitrosomethylaminodiphenyl crystallised readily from benzene in splendid, lustrous, yellow plates which decomposed violently at 187°. On boiling with dilute sulphuric acid, there was vigorous evolution of nitrogen. When this had ceased, water was added and the whole filtered boiling hot. 4-Methylaminodiphenyl sulphate crystallised from the filtrate; the residue, after solution in sodium hydroxide and precipitation, melted at 164° and was identical with 4-hydroxydiphenyl prepared directly from 4-aminodiphenyl. The compound (A) must therefore be 4-diazomethylaminodiphenyl (Found: C, 81.8; H, 5.7; N, 11.1.  $C_{25}H_{21}N_3$  requires C, 82.6; H, 5.8; N, 11.6%).

4-Diazoaminodiphenyl is formed by treating an acetic acid solution of 4-aminodiphenyl with sodium nitrite and forms yellow plates, m. p. 147° (*Ber.*, 1925, 58, 1913).

4-Nitrosomethylaminodiphenyl both alone and when suspended in ether was treated with an alcoholic solution of hydrogen chloride. After 24 hours, the white solid was filtered off and decomposed with sodium hydroxide. The solid thus obtained was dissolved in alcohol, and on cooling, a small crop, m. p. 96°, was obtained. Although crystallisation does not alter this melting point, the product appears to be a mixture of unchanged 4-nitrosomethylaminodiphenyl and 4-methylaminodiphenyl, for, on treatment with acetic anhydride and subsequent crystallisation from alcohol, pure 4-nitrosomethylaminodiphenyl was obtained. After separation of the crop of m. p. 96°, the mother-liquor began to deposit an oil which, after purification, yielded 4-methylaminodiphenyl (m. p. 38°).

*Diphenyl-4-acetylchloroamine*.—4-Acetylaminodiphenyl (31.5 g.) was dissolved in the minimum quantity of boiling alcohol, and the solution stirred rapidly into 3 litres of cold water, a paste of the consistency of whipped cream resulting. This paste was filtered off with the aid of the pump but not pressed out; it was washed with water to remove all alcohol, and then suspended in water (600 c.c.) containing potassium bicarbonate (60 g.). A considerable excess of sodium hypochlorite solution was added [equivalent to 11.6 g. of hypochlorous acid instead of 7.9 g. (calc.)], the strength of the whole mixture being 0.16*N* in respect of hypochlorous acid.

The mixture was maintained at about 70° with constant shaking for  $\frac{1}{2}$  hour, and then allowed to cool. The solid was filtered off and a sample extracted with chloroform. The solvent was removed by a current of air and finally by evacuation. A weighed quantity of this product was dissolved in chloroform and shaken with acetic acid and potassium iodide solution and the liberated iodine was estimated (Found: Cl, 13.9.  $C_{14}H_{12}ONCl$  requires Cl, 14.4%).

This compound crystallises from chloroform-light petroleum in square plates melting at 127° if heated rapidly, and at 160° undergoes a vigorous change, presumably to 3-chloro-4-acetylaminodiphenyl.

*Transformation of Diphenyl-4-acetylchloroamine.*—The main bulk of this substance was filtered off, well washed with water, dissolved in glacial acetic acid, and the solution kept at 80° for 10 minutes and cooled; the vessel then became filled with masses of colourless needles, m. p. 145°, and 147° after recrystallisation from aqueous alcohol. The final mother-liquors contained a little unchanged 4-acetylaminodiphenyl and a trace of a brown oil.

Fractional crystallisation of this substance and of the residues in the acetic acid mother-liquors failed to detect the presence of any trace of 4'-chloro-4-acetylaminodiphenyl. The compound, hydrolysed by boiling 50% sulphuric acid, gave a base which, after crystallisation from aqueous methyl alcohol, melted at 69°. 4'-Chloro-4-aminodiphenyl has m. p. 134°, so that it is highly probable that the above compound is 3-chloro-4-aminodiphenyl, and this view of its constitution is supported by its preparation by direct chlorination.

Chlorine (6.65 g.) (5% excess) was slowly bubbled through a solution of 4-acetylaminodiphenyl (21 g.) in glacial acetic acid (300 c.c.) in a tall vessel. A copious precipitate began to form at once, and after completion of the experiment 50 c.c. of water were added and the pale yellow product was filtered off. It melted at 144° and after recrystallisation from alcohol was obtained in fine, colourless needles, m. p. 146°. This substance on hydrolysis gave a base, m. p. 69°, identical with that obtained above. Exhaustive fractional crystallisation showed that the chlorination was practically quantitative, only 4% of unchanged 4-acetylaminodiphenyl being recovered and no trace of 4'-chloro-4-acetylaminodiphenyl was detected.

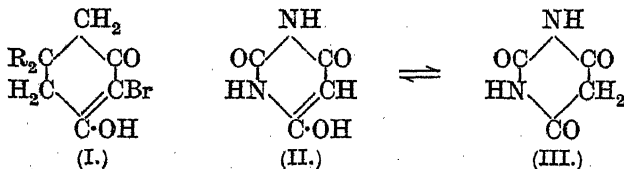
One of the authors (F. B.) gratefully acknowledges receipt of a grant from the Advisory Council of the Department of Scientific and Industrial Research.

CLXI.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XII. Halogen Compounds of Barbituric Acids.*By ALEXANDER KILLEN MACBETH, THOMAS HENRY NUNAN,  
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PREVIOUS work on the halogen derivatives of certain diketones has now been extended to compounds of the barbituric acid series. Baeyer (*Annalen*, 1864, **130**, 133) pointed out that there is a difference in the reactivity of the two halogen atoms in dibromobarbituric acid, one being more readily replaced than the other by hydrogen. Whiteley (J., 1921, **119**, 377) extended this observation and found that the reduction of dibromobarbituric acid is effected to the extent of one-half of the total bromine when an aqueous solution of the compound is added to a neutral solution of potassium iodide.

Hydrazine hydrate has now been found to act in a similar way, nitrogen being liberated in a volume agreeing with the reduction of one bromine atom. Similarly the chlorine atom is removed by this reagent from dichlorobarbituric acid. The corresponding halogen compounds of 1-phenylbarbituric acid and 1:3-diphenylbarbituric acid, as anticipated, gave results in agreement with the above observations, the reduction occurring readily in all cases.

The stability of the monohalogen derivatives of the barbituric acids may be connected with the enolic constitution of these compounds, in accordance with the explanation advanced (J., 1922, **121**, 1117, 2173) in the case of the derivatives of 1:1-dimethyl-*cyclohexane*-3:5-dione and *cyclohexanespirocyclohexane*-3:5-dione (I;  $R_2 = \text{Me}_2$  and  $\text{C}_3\text{H}_{10}$ ), respectively).

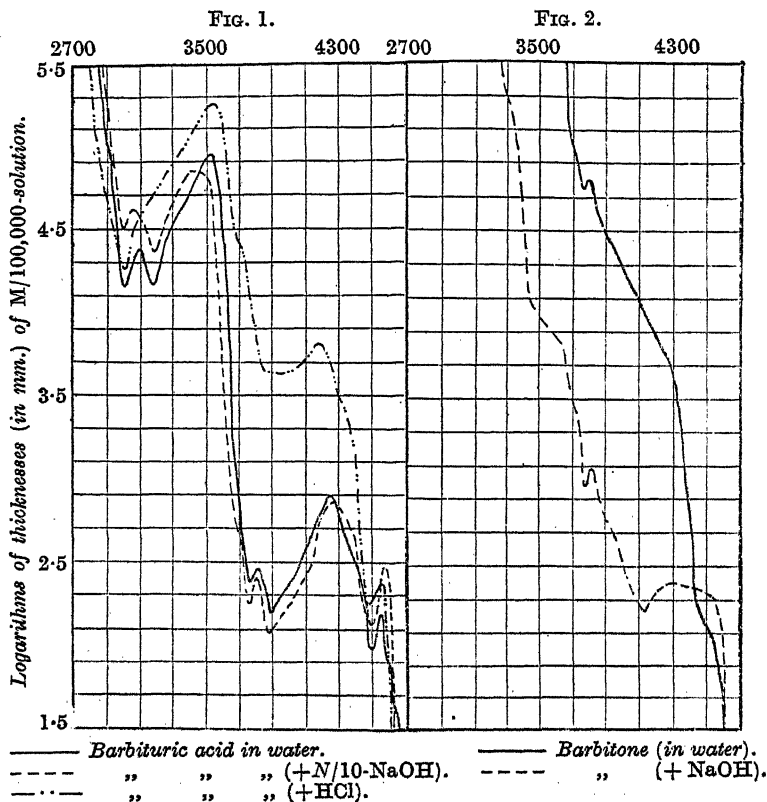


The difference in behaviour of the dichloro-derivatives of barbituric acids and those of the other diketones previously examined (J., 1922, **121**, 1120, 2176; 1923, **123**, 1129) is of interest. In the former case one of the halogen atoms is eliminated by hydrazine hydrate, whereas in  $\gamma\gamma$ -dichloroacetylacetone,  $\gamma\gamma$ -dichlorobenzoylacetone, 4:4-dichloro*cyclohexane*-3:5-dione, and *cyclohexanespiro*-4:4-dichloro*cyclohexane*-3:5-dione no reduction occurs. A ready explanation of this difference is obtained on the polarity basis by



considering the alternate effects of the other atoms in the barbituric acid ring, all of which act together to increase the induced electro-positive character of the halogen atoms.

The stability of the halogen atom in the monohalogenobarbituric acids may, as has been indicated above, be explained by assuming an enolic structure for these compounds. In order to throw further light on this assumption the absorption spectra of characteristic



compounds of this class were examined. The results are shown in Figs. 1—4. The absorption of barbituric acid was examined by Hartley (J., 1905, 87, 1796), who found that the acid transmitted a continuous spectrum very freely through thicknesses of  $M/1000$ -solution varying from 1—20 mm. In view of the results obtained in the past few years in absorption work, we were not surprised to find, on further examination of barbituric acid, that it showed selective absorption, its spectrum being characterised by deep complex bands extending over  $1/\lambda$  2950—3400, 3700—4200, 4450—

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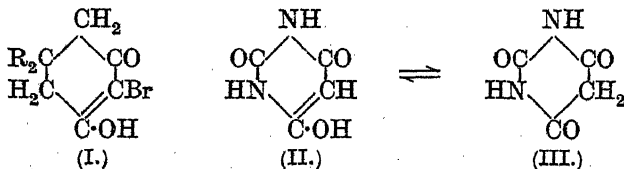
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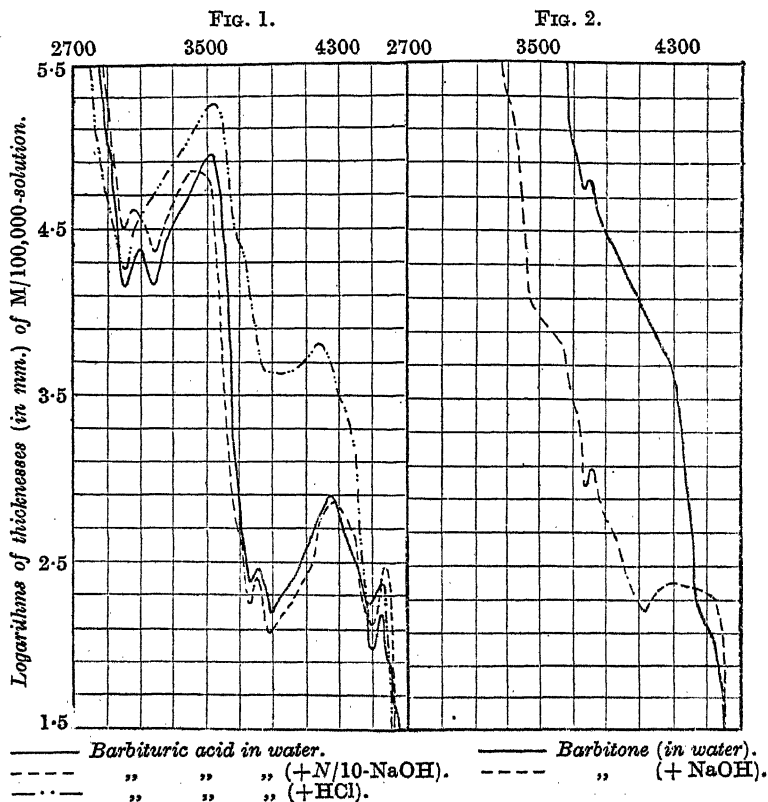
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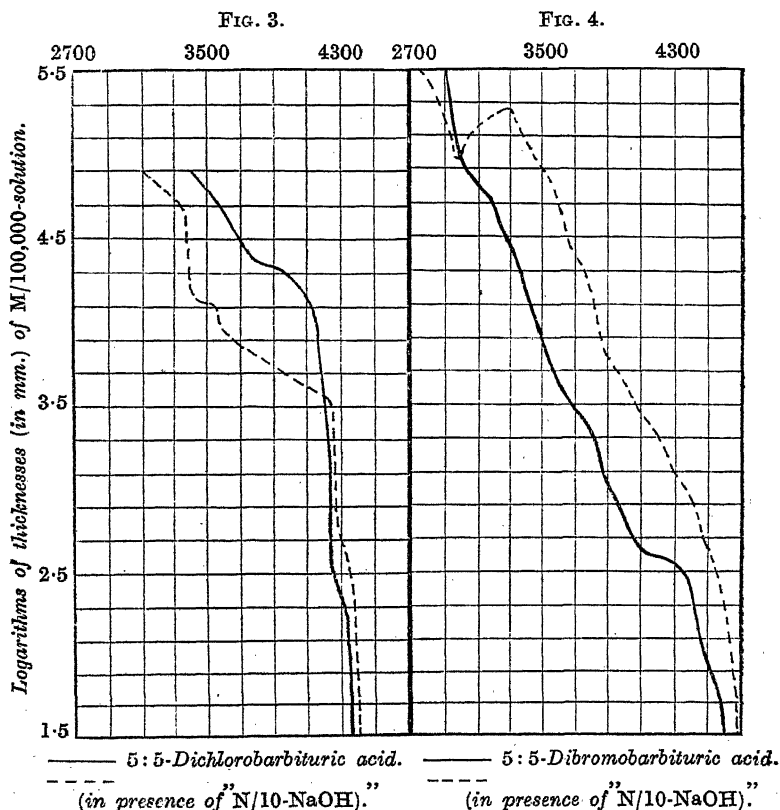
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4530 and with heads at  $1/\lambda$  3000, 3170, 3760, 3880, 4490 approximately. The sodium salt (barbituric acid in the presence of  $N/10$ -sodium hydroxide) shows an absorption practically identical with that of the acid itself and therefore it is evident that in aqueous solution the acid exists in the enolised form (II). As was expected, in the presence of a strong acid the keto-enol change is induced: the absorption curve of barbituric acid in the presence of hydro-



chloric acid does not show to the same extent the marked selective effect characteristic of the enolic structure, the acid being present mainly in the ketonic form (III).

It was considered of interest to examine the absorption of barbitone, as the constitution of this compound is definitely fixed and it may be taken as characteristic of the *C*-dialkyl type. Its spectrum, like that of barbituric acid in the presence of hydrochloric acid, shows no selective effect characteristic of the enolic

form. In the presence of alkali, barbitone further develops the small absorption band at about  $1/\lambda$  3760, and this is probably due to enolisation involving a hydrogen atom of one of the imino-groups.

The absorption spectra of dichloro- and dibromo-barbituric acids are shown in Figs. 3 and 4. The curves are of the same type as those of barbitone, the selective effect connected with the enolic structure being absent. It has been pointed out that hydrazine hydrate reacts with the dihalogen compounds, eliminating one of the halogen atoms and forming the hydrazine salt of the resulting monohalogen derivative. No marked band development is observed in the spectra of the dihalogen compounds on the addition of sodium hydroxide, and therefore it must be inferred that, at the dilutions employed, this reagent does not react greatly with the labile halogen atoms.

The evidence of the absorption spectra of barbituric acid and its derivatives therefore clearly shows (a) that the parent acid exists in the enolic form in aqueous solution, whilst in acid solution the compound is present mainly as the ketonic modification; and, further, (b) that the dihalogen derivatives are compounds of the *C*-dihalogen type, which leaves no grounds for attributing the reactivity of the halogen atom to an oxygen-halogen linking (compare Graham and Macbeth, J., 1922, **121**, 1109, 2601). The bands found in the regions  $1/\lambda$  3000 and 3760 are probably connected with enolisation involving an imino-group, as these are found in barbitone and dibromobarbituric acid in the presence of alkali.

#### EXPERIMENTAL.

The absorption spectra recorded were all obtained with a Hilger spectroscope fitted with a camera attachment. The reductions described were carried out in a Van Slyke nitrometer, hydrazine hydrate (50% solution) being employed throughout.

*Dichlorobarbituric acid.* Barbituric acid, prepared by Gabriel and Coleman's method (*Ber.*, 1904, **37**, 3657), was chlorinated in aqueous suspension at 30–40°, leaflets, m. p. 219–220°, being obtained. The reaction with hydrazine hydrate is vigorous and is complete in a few seconds. 5 C.c. of a solution of 0.980 g. in 25 c.c. of alcohol liberated 11.9 c.c. of nitrogen at 10.5° and 732 mm. One g.-mol. therefore liberates 13.93 g. of nitrogen, corresponding with the removal of one chlorine atom.

The *hydrazide* of monochlorobarbituric acid is precipitated from the above reaction mixture and may also be prepared by the addition of hydrazine hydrate to an alcoholic solution of monochlorobarbituric acid. It does not melt below 300° (Found:

Cl, 18.2;  $N_2H_4$ , 16.7.\*  $C_4H_7O_3N_4Cl$  requires Cl, 18.4;  $N_2H_4$ , 16.6%).

*Dibromobarbituric acid* was prepared by Biltz and Hamburger's method (*Ber.*, 1916, 49, 635). Recrystallised from 2*N*-nitric acid, it had only a faint rose tinge and melted at 234°. A very vigorous reaction takes place with hydrazine hydrate, and white crystals of the hydrazide of monobromobarbituric acid separate. 5 C.c. of a solution of 1.124 g. of the dibromo-compound in alcohol liberate 12.1 c.c. of nitrogen at 15° and 729.1 mm. One g.-mol. therefore liberates 14.07 g. of nitrogen, which corresponds with the reduction of one bromine atom.

The *hydrazide* of monobromobarbituric acid, isolated above, may also be prepared directly from monobromobarbituric acid. It does not melt below 300° (Found: Br, 33.8;  $N_2H_4$ , 13.3.  $C_4H_7O_3N_4Br$  requires Br, 34.0;  $N_2H_4$ , 13.5%).

*Monobromobarbituric acid*, prepared by Biltz and Hamburger's method (*loc. cit.*), showed no reduction with hydrazine hydrate at the laboratory temperature.

5 : 5-Dibromo-1 : 3-diphenylbarbituric acid, prepared by Whiteley's method (*J.*, 1907, 91, 1367), reacts vigorously with hydrazine hydrate with the elimination of one bromine atom. 0.438 G. of the dibromo-compound liberated 12.6 c.c. of nitrogen at 13° and 719.8 mm. on treatment with hydrazine hydrate. One g.-mol. liberates 14.2 g. of nitrogen, which is in fair agreement with the removal of one halogen atom.

The *hydrazide* of 5-bromo-1 : 3-diphenylbarbituric acid separates during the above reaction as a creamy solid which recrystallises from alcohol in small needle-shaped laths; these appear as arborescent aggregates under the microscope; m. p. 220° (Found: Br, 21.6;  $N_2H_4$ , 8.3.  $C_{16}H_{15}O_3N_4Br$  requires Br, 21.8;  $N_2H_4$ , 8.5%).

5-Bromo-1 : 3-diphenylbarbituric acid, prepared by Whiteley's method (*J.*, 1921, 119, 378), was not reduced by hydrazine hydrate, but formed the above hydrazide.

1-Phenylbarbituric acid was prepared on lines parallel to those followed in the preparation of the diphenyl acid. Phosphoryl chloride (60 g.), malonic acid (20 g.), and phenylcarbamide (25 g.) were heated under reflux for 6 hours with dry chloroform (200 c.c.) at a temperature just below the boiling point. After removal of the chloroform in a current of air, the residual syrup was left in alcohol to decompose the phosphoryl chloride and then poured on ice. The solution of the creamy solid in sodium carbonate was filtered, and acidified with hydrochloric acid. The resulting solid

\* Estimated by a modification of Rimini's method (see *J.*, 1925, 127, 897).



was gently heated with a little alcohol to remove the soluble acetylated products, and after crystallisation from alcohol had m. p.  $262^{\circ}$  (Found: N, 13.7.  $C_{10}H_8O_3N_2$  requires N, 13.7%).

**3:3-Dibromo-1-phenylbarbituric Acid.**—Phenylbarbituric acid (5 g.) was heated on a water-bath with glacial acetic acid (50 c.c.) \* and dissolved on the gradual addition of the theoretical amount of bromine. The solution, after further heating (30 minutes), was poured on ice. Repeated crystallisation of the precipitated yellow solid gave almost white, lath-shaped crystals of the dibromo-acid, m. p.  $204^{\circ}$  (Found: Br, 44.0.  $C_{10}H_6O_3N_2Br_2$  requires Br, 44.2%).

The dibromo-acid reacts readily in alcoholic solution with hydrazine hydrate, liberating nitrogen and precipitating the hydrazide of the monohalogen acid. 0.2980 G. liberated 9.8 c.c. of nitrogen at  $16^{\circ}$  and 748 mm. One g.-mol. therefore liberates 13.9 g. of nitrogen, which corresponds with the reduction of one bromine atom.

The *hydrazide* of 3-bromo-1-phenylbarbituric acid, isolated above, forms rectangular needles, m. p.  $146^{\circ}$  (Found: Br, 25.4;  $N_2H_4$ , 10.5.  $C_{10}H_{11}O_3N_4Br$  requires Br, 25.6;  $N_2H_4$ , 10.2%).

**5-Bromo-1-phenylbarbituric Acid.**—The calculated quantity of bromine was added to the parent acid (5 g.), suspended in chloroform (50 c.c.) and warmed on the water-bath. After  $\frac{1}{2}$  hour, the solution was filtered, and the solid crystallised several times from spirit, being thus obtained in faintly pink, crystalline warts, m. p.  $213^{\circ}$  (Found: Br, 28.2.  $C_{10}H_7O_3N_2Br$  requires Br, 28.2%). No reduction took place on treatment with hydrazine hydrate, the above hydrazide being formed.

We (T. H. N. and D. T.) wish to acknowledge a grant from the Department of Scientific and Industrial Research which enabled us to participate in the work.

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\* It is inadvisable to use more acetic acid, as the dibromide is then not precipitated when the solution is subsequently poured on ice.

CLXII.—*The Velocities of the Reactions between Ethyl Iodide and the Sodium Salts of Various Substituted Phenols in Ethyl-alcoholic Solution.*

By LEONARD JAMES GOLDSWORTHY.

ALTHOUGH much work has been done on the relation between the constitutions of different alkyl halides and their activities towards the sodium salts of phenol and of  $\alpha$ - and  $\beta$ -naphthol (Segaller, J., 1913, **103**, 1154, 1421; 1914, **105**, 106, 112; Cox, J., 1918, **113**, 666, 821; 1920, **117**, 493; Shroder and Acree, J., 1914, **105**, 2583), the effects of the substituents in the phenolic substances on the velocities have not hitherto been studied. The object of the present investigation was to ascertain the effect of introducing methyl and chlorine in different positions in the molecule of sodium phenoxide, on the rate of reaction of this substance with ethyl iodide. It was hoped that the results might be of some value in reference to the general and induced polarity effects accompanying substitution in the benzene ring.

As Segaller and others have shown, the reactions between alkyl halides and sodium phenoxides are bimolecular but of a special type, the velocity coefficients being smaller the greater the initial concentrations of the reacting substances, in accordance with the equation  $k_v = k_1 + a \log v$ , where  $v$  is the volume containing 1 g.-mol. of the alkyl halide and sodium phenoxide. All the reactions studied in this investigation were therefore carried out in solutions of the same strength, *viz.*, seminormal, with a view to obtain comparable results.

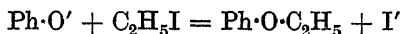
The following are the mean values ( $k \times 10^5$ ) of the observed velocity coefficients for the sodium salts of the cresols and chlorophenols: Concentrations of sodium salts and of ethyl iodide,  $N/2$ . Temp. 42.5°.

(Phenol .....	702)	<i>p</i> -Chlorophenol .....	393
<i>p</i> -Cresol .....	918	<i>o</i> - " .....	334
<i>m</i> - " .....	810	<i>m</i> - " .....	278
<i>o</i> - " .....	726	2:4-Dichlorophenol .....	196

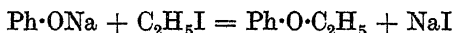
The results resemble those obtained by Boyd and Marle (J., 1914, **105**, 2117) in their investigation on the reactivities of substituted sodium phenoxides towards ethylene and propylene oxides, the order of the reactivities of the cresols and chlorophenols towards ethyl iodide and ethylene oxide being identical.

A possible explanation of the order of the reactivities towards ethyl iodide is suggested by the results obtained by Shroder and Acree in the study of the reactions between sodium phenoxide and

alkyl halides (J., 1914, 105, 2582). They have shown that in a mixture of sodium phenoxide and ethyl iodide in alcoholic solution, the "ionic" and "molecular" reactions



and



occur simultaneously, the former being about five times as fast as the latter. The "ionic" reaction involves the transfer of an electron from the phenoxide ion to the iodine atom, a process which will be the more easily effected the weaker the tendency of the phenoxide ion to hold its electron—in other words, the smaller the ionisation constant of the phenol in question. We should expect, therefore, that the order of the reactivities of the phenoxides would be the inverse of the order of the ionisation constants of the corresponding phenols. The results, except in the case of sodium *o*-tolyl oxide, accord with this expectation, the ionisation constants increasing in the order *o*-, *p*-, and *m*-cresol, phenol, *p*-, *o*-, and *m*-chlorophenol, 2:4-dichlorophenol.\* In the case of sodium *o*-tolyl oxide the retarding steric effect of the methyl group in the ortho-position may account for the unexpectedly low reactivity.

#### EXPERIMENTAL.

The ethyl alcohol used in these experiments was commercial absolute alcohol, carefully dried by digestion with lime and calcium. The ethyl iodide was purified by successive washings with dilute caustic soda solution and water, drying over calcium chloride, and distillation from silver powder. The cresols and chlorophenols, supplied by Kahlbaum, were purified by fractional distillation a few hours before use. All the instruments used were standardised against instruments carrying the certificate of the National Physical Laboratory.

The experiments were carried out at  $42.5^\circ \pm 0.1^\circ$  in a thermostat provided with an Ostwald toluene regulator and an efficient stirrer.

To a weighed quantity of the phenol was added a measured volume of an alcoholic solution containing an equivalent quantity of sodium ethoxide. The solution was then diluted to normal concentration by adding the calculated volume of alcohol. 50 C.c. of this solution

\* The ionisation constants of phenol and the cresols have been determined by Dawson and Mountford (J., 1918, 113, 937). The order of the constants for *p*- and *o*-chlorophenols may be deduced from the measurements of the hydrolysis of their salts by Hantzsch and Farmer (Ber., 1899, 32, 3066, 3089). It is assumed from a consideration of the induced polarity effects that the ionisation constant of *m*-chlorophenol, for which data are not available, is greater than those of *o*- and *p*-chlorophenol.

were mixed quickly with an equal volume of a normal solution of ethyl iodide, and 10 c.c. of the mixture were introduced into each of eight small test-tubes, which had been steamed out previously. The test-tubes, provided with well-fitting rubber stoppers, were then placed in the thermostat. After 10 minutes, the contents of one of the tubes were transferred quickly to a beaker containing ice and an amount of standard acid nearly sufficient to neutralise the unchanged phenoxide. The titration was completed as quickly as possible, with lacmoid as indicator. Further titrations were carried out in a similar way at suitable intervals of time. The results were calculated from the equation  $k = xy/ta(a - x)$ , in which  $y$ ,  $a$ , and  $a - x$  represent the volume (in c.c.) of acid required to neutralise the phenoxide in 10 c.c. of the mixture before the commencement of the experiment, in the first titration (zero-time), and after  $t$  minutes, respectively.

In order to economise space the detailed results of only one experiment are shown, *viz.*, that in which the salt was sodium *m*-tolyl oxide, and *N*/5-hydrochloric acid was used for titration.

$t$ .	$a-x$ .	$x$ .	$k \times 10^5$ .	$t$ .	$a-x$ .	$x$ .	$k \times 10^5$ .
0	22.15	—	—	90	13.45	8.70	811
30	18.15	4.00	829	120	12.05	10.10	788
60	15.40	6.75	824	150	10.80	11.35	791
70	14.70	7.45	817				Mean 810.

In conclusion, the author wishes to express his thanks to Mr. D. H. Peacock for the interest which he has shown in this work and for some useful suggestions.

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### CLXIII.—Carboxylated $\beta$ -Diketones.

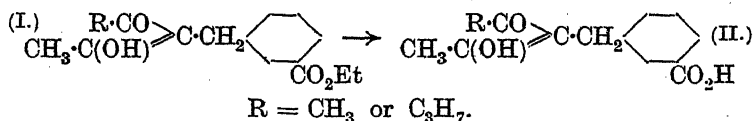
By GILBERT T. MORGAN and CHARLES RAYMOND PORTER.

IN this communication we describe the synthesis of new  $\beta$ -diketones containing auxiliary carboxyl groups, these substances having been prepared with the object of facilitating the resolution of metallo- $\beta$ -diketones into optically active enantiomerides.

Hitherto this separation has been effected only with such salts as  $[\text{CoAc}_2\text{en}]\text{Cl}_2$  and  $[\text{CoPr}_2\text{en}]\text{Cl}_2$ , where Ac and Pr represent the univalent radicals of acetylacetone and propionylacetone respectively (Werner, Schwyzer, and Karrer, *Helv. Chim. Acta*, 1921, 4, 113), but not with metallo- $\beta$ -diketones such as  $[\text{BePr}_2]$  and  $[\text{CuPr}_2]$  or  $[\text{FeAc}_3]$  and  $[\text{CoAc}_3]$ , where the metal is wholly combined with the organic

radical. Even if the two foregoing pairs of metallo- $\beta$ -diketones exist respectively in tetrahedral and octahedral forms, an experimental difficulty arises from the fact that these substances, being non-ionised inner metallic complexes, do not combine either with optically active acids or with alkaloids. Moreover, the examination of selected crystals has not in this series led to positive results.

An auxiliary acidic group has been conferred on acetylacetone by condensing the sodium salt of this  $\beta$ -diketone with *ethyl  $\omega$ -chloro-m-toluate* (*m-carbethoxybenzyl chloride*),  $\text{CH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , when 3-*m-carbethoxybenzylacetylacetone* (I;  $\text{R} = \text{CH}_3$ ) was produced which by hydrolysis in concentrated sulphuric acid furnished 3-*m-carboxybenzylacetylacetone* (II;  $\text{R} = \text{CH}_3$ ), a  $\beta$ -diketone containing two acidic functions, a chelate radical and the carboxyl substituent.



Cobaltic and chromic derivatives of the free carboxy-diketone were prepared but found to be unsuitable for resolutions with optically active alkaloids.

Homologues of the foregoing diketones with unsymmetrical chelate groups were prepared by a similar series of operations carried out on sodium butyrylacetone, when 3-*m-carbethoxybenzylbutyrylacetone* (I;  $\text{R} = \text{C}_3\text{H}_7$ ) resulted, and this ester on hydrolysis yielded 3-*m-carboxybenzylbutyrylacetone* (II;  $\text{R} = \text{C}_3\text{H}_7$ ).

The free carboxy-diketone (II;  $\text{R} = \text{C}_3\text{H}_7$ ) gave a green dicupric salt convertible into a grey monocupric derivative the colour of which suggested (Morgan, Drew, and Porter, *Ber.*, 1925, 58, 333) that the metal was held in the chelate group, but, although soluble in organic media, the monocupric compound rapidly decomposed in warm solutions into dicupric salt and carboxy-diketone.

A similar pair of beryllium derivatives was prepared, the monoberyllium compound being soluble in organic media, but crystallisation of this substance was impossible because of its rapid decomposition into ill-defined, insoluble products. Moreover, the alkaloidal salts of this monoberyllium derivative were also unsatisfactory and afforded no indication of any resolution.

Both carboxy- $\beta$ -diketones exhibit keto-enol isomerism: specimens crystallised from non-hydroxylic solvents such as benzene or petroleum were more fusible and gave immediately with ferric chloride purple colorations, thus indicating the enolic variety, whereas preparations crystallised from alcohol were less fusible

and developed the coloration only gradually, thereby suggesting a diketonic modification.

#### EXPERIMENTAL.

*Ethyl  $\omega$ -chloro-*m*-toluate* (*m*-carbethoxybenzyl chloride) was prepared by a modification of the patented method (E.P. 29720/1910; D.R.-P. 234913; Friedländer's "Fortschritte," X, p. 117). *m*-Toluic acid (100 g.) was gradually warmed to 120° with 75 c.c. of thionyl chloride and thereby converted into *m*-toluoyl chloride, b. p. 105°/20 mm. Chlorine was passed into 112.5 g. of this chloride at 160—180° until its weight increased to 138 g. The resulting  $\omega$ -chloro-*m*-toluoyl chloride was warmed gently with 50 c.c. of alcohol; a vigorous reaction set in with evolution of hydrogen chloride, the flask being finally heated to 140°. The ester was washed rapidly with dilute aqueous sodium carbonate and water, dried, and distilled under reduced pressure; 130 g. (= 89%) were obtained boiling at 140—150°/12 mm. (Found: Cl, 18.4.  $C_{10}H_{11}O_2Cl$  requires Cl, 17.9%).

I. 3-*m*-Carbethoxybenzylacetylacetone (I; R =  $CH_3$ ).—Eighty g. of sodium acetylacetone and 130 g. of the foregoing ester were heated together under reflux at 135—145° for 3 hours and finally at 160°. The cooled product was extracted with water and ether; the dried ethereal layer was distilled, yielding acetylacetone and 84 g. of a higher fraction, b. p. 175—215°/11 mm. The less volatile fraction dissolved in alcohol and was added to aqueous copper acetate containing an equivalent proportion of ammonia. After 2 or 3 days the copper derivative was collected, and washed with dilute acetic acid to dissolve copper hydroxide and with ether to remove liquid impurities. The ethereal washings were worked up again with further distillations of crude diketone.

*Copper 3-m-carbethoxybenzylacetylacetone*, a light grey, micro-crystalline powder, was insoluble in water but soluble in organic solvents; it crystallised from benzene and melted at 173—176° (Found: C, 61.3; H, 5.6.  $C_{30}H_{34}O_8Cu$  requires C, 61.6; H, 5.8%).

On extraction with dilute sulphuric acid and ether 67 g. of this copper salt yielded 42 g. (= 70%) of the liquid diketone, b. p. 209—215°/12 mm., which developed a reddish-purple coloration with alcoholic ferric chloride.

*Acidic Hydrolysis of 3-m-Carbethoxybenzylacetylacetone*.—The ester was not affected by boiling with 5*N*-sulphuric acid, 40% sulphuric acid, concentrated hydrochloric acid, or glacial acetic acid. Heating with syrupy phosphoric acid led to products giving no coloration with ferric chloride.

A solution of 1 or 2 g. of the ester in 3 or 4 volumes of concentrated

sulphuric acid was heated on the water-bath; hydrolysis occurred and the cooled red liquid yielded a white solid when poured on to crushed ice. This product was crystallised from benzene or benzene-petroleum. The first mother-liquors contained unchanged carboethoxy- $\beta$ -diketone, which was recovered and worked up in subsequent batches.

3-*m*-Carboxybenzylacetylacetone (II;  $R = CH_3$ ), obtained by this hydrolysis in 50% yield, crystallised from alcohol in colourless needles, m. p.  $130^\circ$ , and from benzene in white needles, m. p.  $115^\circ$ . The change in melting point is reversible and is probably due to keto-enolic isomerism. A specimen crystallised from benzene gave with ferric chloride a purple coloration, whereas the preparation from alcohol developed this colour only after a time (Found: C, 67.1; H, 5.8.  $C_{13}H_{14}O_4$  requires C, 66.7; H, 6.0%).

3-*m*-Carboxybenzylacetylacetone was fairly stable in acid solution but readily hydrolysed by alkalis (p. 1261). It was soluble in ordinary organic solvents except light petroleum and dissolved sparingly in water.

*Copper Derivatives of 3-m-Carboxybenzylacetylacetone.*—A bluish-green precipitate separated on adding excess of aqueous copper acetate to an acetone solution of 3-*m*-carboxybenzylacetylacetone. This dicupric salt containing copper attached both to carboxyl and chelate groups (Cu, 21.7.  $C_{26}H_{24}O_8Cu_2$  requires Cu, 21.5%) was insoluble in the ordinary organic solvents excepting pyridine, in which it dissolved extremely readily. On concentrating the pyridine solution, a precipitate was formed which lost pyridine on drying and reverted to the original dicupric salt. This substance developed slowly a red ferric chloride coloration, decomposed to a brown paste at  $250^\circ$ , and lost half its copper on trituration with an equivalent proportion of *N*/10-sulphuric acid, yielding a light grey monocupric derivative (Cu, 11.9.  $C_{26}H_{26}O_8Cu$  requires Cu, 12.0%), which decomposed at  $235$ – $240^\circ$  to a brown paste. It was insoluble in all ordinary solvents, and with ferric chloride it developed a red coloration only after a few minutes. This slowness of reaction and the grey colour suggest that the copper of the monocupric salt is attached to the chelate group.

*Other Metallic Derivatives.*—Normal beryllium acetate added to an acetone solution of the 3-*m*-carboxybenzylacetylacetone produced a white precipitate of beryllium derivative insoluble in organic solvents. A portion of the beryllium could be removed by trituration with dilute sulphuric acid (one equivalent) and the residue was then soluble in organic media, but it could not be purified by crystallisation because it reverted to a mixture of free diketone-carboxylic acid and the diberyllium derivative of this acid.

The dark green chromium derivative, although soluble in chloroform, was transformed in the warm solution into an insoluble green vitreous mass.

II. 3-*m*-Carbethoxybenzylbutyrylacetone (I;  $R = C_3H_7$ ).—Butyrylacetone prepared from methyl propyl ketone and ethyl acetate (Morgan and Drew, J., 1924, 125, 737) was dissolved in 10 volumes of dry cold ether and converted into its sodium salt by the addition of sodium in thin slices. After collecting the separated sodium derivative, the mother-liquors were concentrated, the total yield being practically quantitative. A mixture of 110 g. of sodium butyrylacetone and 145 g. of 3-*m*-carbethoxybenzyl chloride was heated under reflux in an oil-bath. At 140–150°, the sodium salt dissolved to a clear liquid and sodium chloride separated. After an hour at 160°, the cooled product was extracted with ether and water. The ethereal layer was washed with dilute acetic acid and distilled under reduced pressure. Butyrylacetone passed over first, yielding 25 g. of its copper derivative, and a higher fraction was obtained boiling above 180°/10 mm. The less volatile portion, dissolved in alcohol, was treated with excess of aqueous copper acetate containing one equivalent proportion of ammonia. After a few days, the mixture was slightly acidified and the copper derivative collected and washed successively with light petroleum and ether. The grey copper derivative, when extracted with dilute sulphuric acid and ether, regenerated the diketone, b. p. 200–201°/6 mm. (yield 47 g. or 22%).

Copper 3-*m*-carbethoxybenzylbutyrylacetone was soluble in chloroform or benzene and crystallised from the latter as a light grey, microcrystalline powder, m. p. 168–170° (Found: C, 63.6; H, 6.6.  $C_{34}H_{42}O_8Cu$  requires C, 63.6; H, 6.5%).

3-*m*-Carboxybenzylbutyrylacetone (II;  $R = C_3H_7$ ).—The foregoing ester was hydrolysed in 1 to 2 g. lots by mixing with 3 or 4 volumes of concentrated sulphuric acid, the solution being stirred for 2 to 3 minutes on the water-bath. The cooled yellow solution was then poured on to crushed ice and the white solid crystallised as quickly as possible from carbon tetrachloride (yield 50%).

This diketonic acid was more soluble and less stable than its lower homologue from acetylacetone, the crude material being decomposed completely on boiling for more than a few minutes with solvents. It was readily soluble in these organic media and dissolved sparingly in water. When crystallised from aqueous alcohol, the diketo-acid separated in small plates sintering at 80° and melting indefinitely at 100–112°. The purple ferric coloration developed only slowly with this specimen. But a preparation crystallised from benzene-petroleum melted at 78–90° and gave



the ferric coloration immediately (Found : C, 69.1; H, 6.9.  $C_{15}H_{18}O_4$  requires C, 68.7; H, 6.8%).

*Copper Derivatives of 3-m-Carboxybenzylbutyrylacetone.*—Dicupric 3-m-carboxybenzylbutyrylacetone was obtained as a bluish-green precipitate by adding copper acetate to an acetone solution of the diketo-acid. On washing with acetone, a portion dissolved and monocupric derivative was recovered from this extract. The insoluble dicupric salt decomposed to a brown paste when heated above  $225^\circ$  (Found : Cu, 19.4, 19.8.  $C_{30}H_{32}O_8Cu_2$  requires Cu, 19.6%).

*Monocupric 3-m-carboxybenzylbutyrylacetone*, prepared as a grey powder by triturating the foregoing copper compound with *N*/10-sulphuric acid, was soluble in alcohol or acetone, but crystallisation had to be effected as rapidly as possible because the substance decomposed on boiling the solution, with formation of the free diketo-acid and dicupric compound. The monocupric compound sintered at  $173^\circ$  and melted to a green liquid at  $176$ – $178^\circ$  (Found : Cu, 11.1.  $C_{30}H_{34}O_8Cu$  requires Cu, 10.9%).

*Beryllium Derivatives of 3-m-Carboxybenzylbutyrylacetone.*—On mixing an acetone solution of 3-m-carboxybenzylbutyrylacetone with aqueous normal beryllium acetate a copious white precipitate was obtained insoluble in water and the ordinary organic solvents, thus corresponding in properties with the foregoing dicupric salt. This insoluble beryllium compound was triturated with a very slight excess of 2*N*-sulphuric acid, and the mixture filtered. The filtrate contained beryllium; the precipitate was now soluble in organic media. This soluble beryllium derivative could not, however, be crystallised, as its solutions in benzene or other organic solvents rapidly underwent chemical change with the formation of a gelatinous white precipitate.

Numerous attempts were made to prepare the morphine, cinchonidine, brucine, and strychnine salts of the foregoing soluble beryllium derivative, but the products were ill-defined, uncrystallisable, vitreous, or oily substances from which no definite evidence as to resolution could be deduced.

III. *m*-Carboxybenzylacetone or  $\omega$ -Acetonyl-*m*-toluic Acid,  $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ .—On warming with dilute aqueous sodium hydroxide, *m*-carbethoxybenzylacetylacetone or *m*-carbethoxybenzylbutyrylacetone dissolved to a colourless solution from which acids precipitated a white solid soluble in ether. This product, which was also obtained by alkaline hydrolysis of *m*-carb-oxybenzylacetylacetone and *m*-carboxybenzylbutyrylacetone, was identified as *m*-carboxybenzylacetone. It was slightly soluble in water, but dissolved readily in organic media, crystallising therefrom on addition of light petroleum; it also separated from the latter

solvent in lustrous plates, m. p.  $77^{\circ}$  (Found: C, 68.5; H, 6.4.  $C_{11}H_{12}O_3$  requires C, 68.7; H, 6.2%). The equivalent weight by alkalimetry was 194; theory requires 192.

IV. 3-*o*-Carbethoxybenzylacetylacetone,



—*o*-Toluoyl chloride, obtained in practically quantitative yield from *o*-toluic acid and phosphorus trichloride at  $120$ – $170^{\circ}$ , was subjected to a stream of chlorine at  $160$ – $180^{\circ}$  without a catalyst until the calculated increase in weight had been attained. The resulting  $\omega$ -chloro-*o*-toluoyl chloride boiled at  $129$ – $133^{\circ}/12$  mm.

When treated with a slight excess of warm alcohol, this chloride was esterified with loss of hydrogen chloride. The ethyl  $\omega$ -chloro-*o*-toluate was washed with dilute aqueous sodium carbonate, dried, and distilled in small quantities, when the ester boiled at  $139$ – $143^{\circ}/12$  mm.

When larger quantities were distilled, after a portion of the ester had passed over, a solid product collected in the condenser which was identified as phthalide, m. p.  $73^{\circ}$  (Found: C, 71.9; H, 4.6. Calc.: C, 71.6; H, 4.5%).

Ethyl  $\omega$ -chloro-*o*-toluate was condensed with sodium acetylacetone as in the case of the  $\omega$ -chloro-*m*-toluate (p. 1258).

3-*o*-Carbethoxybenzylacetylacetone was obtained by acidifying its grey copper derivative (m. p.  $168$ – $170^{\circ}$ ); it boiled at  $196^{\circ}/14$  mm. and gave a reddish-purple coloration with ferric chloride (Found: C, 68.6; H, 7.1.  $C_{15}H_{18}O_4$  requires C, 68.7; H, 6.9%).

In the distillation of the foregoing diketone, a solid (Found: C, 73.75; H, 5.15%) of higher boiling point came over after the diketone. This product was obtained crystalline by adding petroleum to its benzene solution.

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## CLXIV.—A Comparison of the Atomic Weights of Silicon from Different Sources.

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RESULTS obtained in a recent redetermination of the atomic weight of boron (Briscoe and Robinson, J., 1925, 127, 696) indicated that the value varies slightly with the source of supply. The values

10.818, 10.825, and 10.841 found for Asiatic, Tuscan, and Californian material respectively were tentatively explained as due to variation in the isotope ratio. This paper reviewed the evidence and stated the conclusion that, despite excellent work supporting the opposite contention, there was no inherent improbability in this suggestion. It is to be deplored that much of the earlier work on atomic weights has been on material of unspecified origin, as this makes the discrepancies valueless for statistical investigation. The necessity for further work on boron being obvious, the problem was attacked by comparing the densities of boric oxide from these and other sources. The results of this investigation supported the original conclusion (Briscoe, Robinson, and Stephenson, this vol., p. 70).

Late in 1924, Jaeger and Dijkstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 290; *Z. anorg. Chem.*, 1925, 143, 233) showed that the densities of tetraethylsilane indicated no difference in the atomic weight of silicon exceeding 0.019 unit, which corresponds to a density difference of 0.00010 unit—a remarkable degree of accuracy for the pycnometer method employed. The inconclusive character of these results (see Briscoe and Robinson, *Nature*, 1926, 117, 377) led us to proceed with the redetermination of the atomic weight of silicon projected early in 1924 for the reasons given below.

A brief comparison of the geological occurrence of boron and silicon is appropriate here. Boron is widely distributed and forms about 0.001% of the earth's crust (Clarke and Washington, *Proc. Nat. Acad. Sci.*, 1922, 8, 108). It is found primarily in tourmaline and datolite, from which it is liberated and subsequently concentrated, principally as calcium salts, by the drying up of lakes as in the Asiatic and American deposits, or artificially separated from the steam of fumaroles as at Volterra. Clearly, in each case the boron has been associated for a considerable period with the area in which it is found. Silicon, next to oxygen the most abundant element, occurs terrestrially to the extent of 25.80% (Clarke, "Data of Geochemistry," 1920, 30). The transportation of siliceous material is almost entirely by mechanical means and then only over short distances, which makes it probable that silicon has remained associated with the continental mass on which it is found for considerable geological periods. This would appear to be the case even if Wegener's displacement theory should eventually be substantiated. Thus boron and silicon, for different reasons, have probably retained for great periods of time their general relationship to that area of the earth's surface on which they are found.

Silicon presents certain well-known general chemical similarities

to boron, and, occurring as it does in three isotopic forms, Si = 28, 29, 30 (Aston, *Phil. Mag.*, 1920, 40, 628: Si = 30; confirmed, *Nature*, 1924, 114, 273), appears to be a suitable element for the further investigation of the constancy of atomic weight.

Determinations of the atomic weight of silicon previous to 1920, fully discussed by Clarke (*Mem. Nat. Acad. Sci.*, 1920, 16, 22), are tabulated below (Table I) together with more recent work, under the three heads: halide: silver ratio, halide: oxide ratio, and vapour density.

TABLE I.

*Halide: Silver Ratios.*

Pelouze, <i>Compt. rend.</i> , 1845, 20, 1047 .....	28.370
Dumas, <i>Annales</i> , 1860, 113, 31 .....	28.077
Schiel, <i>ibid.</i> , 1861, 120, 94 .....	27.945
Baxter, Weatherill, and Holmes (preliminary paper), <i>J. Amer. Chem. Soc.</i> , 1920, 42, 1194 .....	28.111
Baxter, Weatherill, and Scripture, <i>Proc. Amer. Acad. Arts Sci.</i> , 1923, 58, 245 .....	28.063, 28.061
Hönigschmid and Steinheil, <i>Z. anorg. Chem.</i> , 1924, 141, 101...	28.105

*Halide: Oxide Ratios.*

Thorpe and Young, <i>J.</i> , 1877, 51, 576 .....	28.381
Becker and Meyer, <i>Z. anorg. Chem.</i> , 1905, 43, 251 .....	28.231
Meyer, <i>ibid.</i> , 1905, 46, 45 .....	28.231

*Vapour Density.*

Jaquerod and Tourpaian, <i>J. Chim. phys.</i> , 1913, 11, 269 .....	28.496
Germann and Booth, <i>ibid.</i> , 1917, 21, 81 .....	28.306

The only values in this table which merit serious consideration from the point of view of high accuracy, as distinct from mere novelty of method, are the more recent halide: silver results. The hope that the comparatively simple and direct halide: oxide ratio might produce results of high accuracy is evidently not realised, probably on account of the difficulty of dehydrating the oxide. Reinvestigation of the method with the facilities now available might more nearly fulfil anticipations. The vapour density determinations are open to criticism on the lines suggested by Clarke (*loc. cit.*). The halide: silver ratios exhibit considerable variation, 27.945—28.370, although the four more recent values are in agreement to 1 part in 560 parts. They lie—though probably by that chemist's happy accident—on either side of Dumas's figure. There is a considerable discrepancy between Baxter's (*loc. cit.*) 1920 preliminary and 1923 final figures, *viz.*, 1 part in 550 parts. The International Committee (*J. Amer. Chem. Soc.*, 1925, 47, 597) have given 28.06 as the rounded mean in spite of Hönigschmid's (*loc. cit.*) 28.105. Clearly, further investigation is required if the atomic

weight of silicon is to be known to a greater accuracy than about 1 part in 700 parts.

*Outline of the Present Investigation.*

With the element silicon the choice of a suitable compound for equivalent determination is limited to the halides, and of these the tetrachloride is certainly the most convenient. The silicates are indefinite in composition; the organic compounds, while occasionally of suitable stability and constancy of composition, are difficult to analyse with the required precision; and the oxide, into which a number of compounds may readily be converted, presents difficulties which have already been commented upon. Furthermore, the tetrachloride readily lends itself to a comparison of the atomic weights of material from different sources, provided a suitable method can be devised for the determination of its density with sufficient accuracy.

Silicon tetrachloride was prepared by chlorinating ferrosilicon, manufactured from silica, in one case from an unknown source, and in four others from known localities in Canada, the United States of America, Sweden, and France. As no British ferrosilicon of known origin was available, silicon was prepared from a Scottish pegmatite, and this was chlorinated. The sample of unknown origin was used in a purely preliminary manner to establish methods employed in the preparation, handling, and purification of the compound. About equal amounts of the five samples of known origin were prepared and they were individually subjected to a rigorous, but strictly uniform, process of purification. When pure, the density of each was determined by the use of glass floats calibrated as to density with extreme accuracy. The constancy of the molecular volume of the chlorides of the various isotopes being assumed, the apparent atomic weights were thus compared.

*The Preparation of Silicon Tetrachloride.*

*Sources of Material.*—Of the methods available for preparing silicon tetrachloride, the most convenient for producing it in quantity without using elementary silicon is that involving the chlorination of ferrosilicon, originally described by Warren (*Chem. News*, 1892, 66, 112). Inquiries were therefore instituted into the production of ferrosilicon in various countries. The materials used were selected from samples from Europe and America, the final choice depending on the geographical locality and the geological age of the silica used in the manufacture (Table II). A British sample was thought desirable, and the pegmatite mentioned below was used as a source of elementary silicon.

TABLE II.

*Europe.*

- (a) 91.2% Ferrosilicon, smelted by the Gullspangs Elektrokemiska Aktiebolag, at Gullspang, Sweden, from quartzite obtained at Anenaset, W. of Lake Animmen, Sweden.
- (b) 75% Ferrosilicon, smelted by Keller and Leleux, at Usine de Livet, Isère, from quartzite obtained at Bourg St. Maurice, Haute Savoie, France.
- (c) Pegmatite from a vein 4.5 miles W. of Strontian, Scotland.

*America.*

- (a) 50% Ferrosilicon, smelted by the Southern Ferro Alloys Company, Chattanooga, Tenn., from silica obtained from the sandstone cap of Lookout Mountain, Alabama, U.S.A.
- (b) 90% Ferrosilicon, smelted by the Union Carbide and Carbon Products Company, Niagara Falls, from quartzite obtained at Killarney, Ontario, Canada.

The authors wish to record their grateful thanks to these and other firms and individuals in various parts of the world who have made this investigation possible by so courteously placing material and information at their disposal.

*Preparation of Silicon Tetrachloride from Ferrosilicon.*—Warren's method (*loc. cit.*) was subsequently elaborated by Martin (J., 1914, 105, 2836), but preliminary experiments showed that these complications were largely unnecessary in the present case. Chlorination of the ferrosilicon was carried out in iron tubes 3 ft. by 1.5 in. which were dried by twice heating to redness in a combustion furnace and cooling with dry air passing through them. After a run they were thoroughly washed and redried, but the majority of the tubes were perforated after two, and none lasted beyond three, chlorinations. Ferrosilicon as a coarse powder retained on a 40-mesh sieve was found to be most suitable. This was obtained by crushing the material in a Weatherhead mill; it was then dried, at 110°, in charges of 200—300 g. immediately before being put into the tubes. The iron tube was heated by a silica-tube resistance furnace. Chlorine from a cylinder was led through two sulphuric acid wash-bottles, past a T-piece manometer dipping 8 inches into frequently renewed sulphuric acid, to the reaction tube. The products were led through an adapter into a clean dry receiving bottle, cooled in a freezing mixture and fitted with an exit tube leading to a ventilator shaft. A rapid stream of chlorine was passed through the heated tube, and after 25 minutes the production of silicon tetrachloride began, and when the rate of production diminished fresh ferrosilicon was exposed to the action of the gas by rotating the tubes slightly and tapping them. Occasional slight back-pressure, due to ferric chloride, was relieved in this way, but after 2.5—3.5 hours the tubes choked up completely and thus ended the run. About 700 c.c. of crude product were obtained from each source and

hermetically sealed by closing the bottle with a tied-in waxed cork.

*Preparation of Silicon Tetrachloride from Pegmatite.*—The pegmatite was rich enough in silicon to be treated as an impure specimen of the oxide, and was reduced with aluminium in the presence of sulphur (Holleman, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, 1, 189; Kuhne, D.R.-P. 147871). 200 G. of finely ground mineral were very thoroughly mixed with aluminium powder (200 g.) and flowers of sulphur (250 g.), charged into a No. 6 Battersea crucible, covered with a layer of sulphur, and fired by means of magnesium ribbon set in a primer of magnesium powder and barium peroxide. Immediately following the reaction, the hot crucible was plunged into water, the aluminium sulphide being thus decomposed, leaving nodules of crystalline silicon. These were washed, dried, crushed, and finely ground in a Weatherhead mill, and this powder was treated with concentrated hydrochloric acid, when there was a marked evolution of gas and a smell suggestive of a silicide. The wash-acid was heated to boiling, cooled, diluted with water and filtered through a Buchner funnel with the aid of a pump. The resulting moist mass was digested with 1 : 2 hydrochloric acid for some time, again filtered, well washed in the funnel, and dried at 110°. 300 G. of silicon as a fine, dark grey powder were obtained from nine reductions.

About 30 g. of this material were placed in a clean dry Jena glass tube of 0.75 in. bore and chlorinated as described for ferro-silicon. The silicon glowed during the chlorination and a small quantity of white residue remained. About 700 c.c. of product were obtained and bottled as before.

*Rough Fractionation of Crude Silicon Tetrachloride.*—This step was introduced to rid the crude product of most of its chlorine and all its solid impurities. The cork of the bottle containing the crude material was replaced by a waxed cork, provided with a short wide delivery tube, which was already connected by means of rubber to a specially constructed fractionating column, 2 ft. long, filled with glass beads. The bottle was carefully heated by a water-bath, and a small head fraction carrying most of the chlorine was allowed to go entirely to waste. A head fraction of about 70 c.c. was now collected in a small bottle cooled in a freezing mixture and, as the last third of this fraction ran colourless, it was concluded that the bulk of the chlorine had been removed. A main fraction of about 600 c.c. was then collected in a dry litre bottle, containing 40 c.c. of pure mercury: it was stoppered as previously described. A slight flouring of the mercury in the case of each main fraction indicated that a trace of chlorine was still

present. The tail fractions subsequently yielded specimens of the hexachloride (b. p.  $141.5^{\circ}$ ), and a fraction of higher boiling point that could not be driven up the column, which was, presumably, the octachloride. The amounts of higher chlorides found were less than those obtained by Martin (*loc. cit.*) in his carefully regulated chlorinations.

#### *Purification of Silicon Tetrachloride.*

The importance of a rigorous purification need hardly be stressed. The crude material possibly contained :

Chlorine .....	b.p. $-34^{\circ}$	Disilicon hexachloride .....	b.p. $145^{\circ}$
Hydrochloric acid .....	$-83$	Trisilicon octachloride .....	212
Phosphorus trichloride .....	76	Antimony trichloride .....	226
Arsenic trichloride .....	130		

Silicon dioxide and its hydrates are probably only very slightly volatile in the vapour of silicon tetrachloride.

Of these compounds, only phosphorus trichloride was likely to persist, but it has a boiling point  $16.5^{\circ}$  above that of silicon tetrachloride. The methods available for purifying the liquid were fractional crystallisation and distillation, and contact with mercury and sodium. Fractional crystallisation was originally part of the scheme, but, unfortunately, became impossible by reason of the increased difficulties experienced in obtaining supplies of liquid air. The means available were thus fractional distillation and prolonged contact with liquid sodium amalgam. They were conducted in the following stages (see Fig. 1, where T, H, and M represent tail, head, and main fractions respectively) :

1. Rough fractionation through a single-column still.
2. Standing for 6 months over mercury, with frequent shakings.
3. Systematic fractional distillation in four stages, conducted in dry air at about atmospheric pressure in an all-glass four-column still.
4. Standing with frequent shakings for upwards of 2 months over sodium amalgam.
5. Fractional distillation into five fractions in a vacuum.
6. Fractional distillation into five fractions in a vacuum.

*Main Fractionation of Silicon Tetrachloride at Atmospheric Pressure.*—This was conducted in a 4-column still (Fig. 2) of Durosil glass similar in principle to that used in the purification of boron trichloride by Briscoe and Robinson (*loc. cit.*). Each piece of the apparatus\* was cleaned with chromic-nitric acid, washed with water, rinsed with pure alcohol, and allowed to drain. The parts

\* Our thanks are due to Mr. G. Ellison of this department for making the individual pieces of glass-ware used in this investigation.



were then assembled and dried by passing dry air in at M and out through  $T_1$  for 3 days, the mercury in the valves sealing the apparatus from outside air. The capillary of the special joint was then sealed, and freshly-made sodium amalgam was filtered into M by means of a long-stemmed funnel. All exit tubes were bent to point downwards, so that any liquid condensing in the phosphorus pentoxide guard-tubes was unable to return to the apparatus.

About 600 c.c. of the roughly-fractionated crude product, after standing over mercury with repeated shaking for 5–6 months, were distilled into  $B_1$ , which was cooled in ice-cold water, leaving

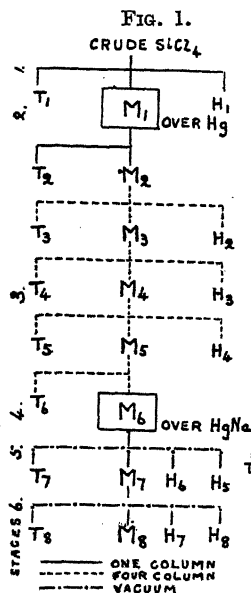
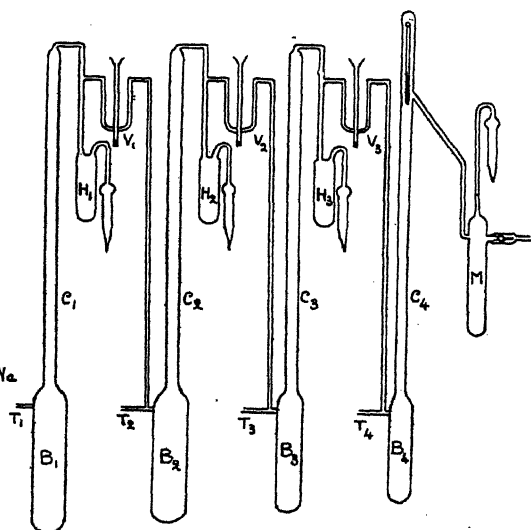


FIG. 2.



behind a tail fraction of 20 c.c. A paper jacket containing solid carbon dioxide kept the base of  $C_1$  cool, while extra mercury which had been poured into  $V_1$  cut off connexion between  $B_1$  and  $B_2$ .  $T_1$  was then sealed off.  $B_1$  was gently warmed with a soft flame, as this method of heating gave steady boiling, and a head fraction of about 50 c.c. was distilled into  $H_1$  which was cooled in solid carbon dioxide. This head fraction was sealed off, mercury was run from  $V_1$  to establish connexion with  $B_2$ , and a main fraction of about 500 c.c. was distilled forward into  $B_2$ , which was cooled in iced water, the base of  $C_2$  being jacketed with solid carbon dioxide. More mercury was poured into  $V_1$  and the tip of  $T_1$  was broken under rubber to connect with a phosphorus pentoxide tube, thus establishing equal pressures at both sides of the valve. A tail of

about 50 c.c. remained in  $B_1$ . Similar head and tail fractions were rejected in distillations from  $B_2$  and  $B_3$ , resulting in 300 c.c. of material in  $B_4$ . The liquid in  $B_4$  was then distilled forward past the thermometer into M (cooled in solid carbon dioxide) where it was sealed up. About 25 c.c. of liquid returned to  $B_4$  on account of column capacity.

To prepare the apparatus for the next distillation the tails and drainings from the columns were distilled from the various boilers by opening the side-tubes  $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$ , after which these side-tubes were sealed up and dry air was passed completely through the apparatus for 3 or 4 days with occasional warmings, thus removing the last traces of silicon tetrachloride: the new head-bulbs were then fused on, and the apparatus carefully dried for the next sample.

*The Boiling Point of Silicon Tetrachloride.*—This is a useful criterion of purity, and it was measured with all the accuracy possible under the conditions of the experiment. The thermometer used (range  $10-60^\circ$ ) was subsequently compared with the N. P. L. thermometer mentioned below, and was usually less than  $0.02^\circ$  in error. Temperatures, which remained fairly steady, were taken at short intervals, any fluctuations being traceable to variations in the rate of distillation which caused slight pressure changes in the system. There was absolutely no tendency towards a rise of temperature during the last stages of each distillation. Table III gives the mean boiling point and atmospheric pressure for each sample.

TABLE III.

Sweden .....	$57.10^\circ$	761.6 mm.	France.....	$56.83^\circ$	753.9 mm.
Scotland .....	$56.95$	758.0 mm.	Canada .....	$56.91$	756.0 mm.
U.S.A. ....	$57.12$	763.3 mm.			

This indicates a boiling point between  $57.02^\circ$  and  $57.05^\circ$  at 760 mm., a figure in fair agreement with the  $56.9^\circ$  of Becker and Meyer (*loc. cit.*) and the  $56.8^\circ$  of Stock, Somieski, and Wintgen (*Ber.*, 1917, 50, 1754).

[*Special Note on the French Fraction.*—A few days after distillation the vessel containing the main fraction of the French material from the 4-column still developed an extensive series of cracks round the upper portion near the special joint. Since there was no apparent entry of air into the container, it was painted over with thick collodion varnish, bound with pure rubber tape and finally painted with a viscous solution of pure rubber. After standing for some days, it was joined to a new, clean, dry special-joint container provided with fresh sodium amalgam, the strains between the two vessels being relieved by a number of right-angle

bends in the thin-walled connecting tube. The special joint was then broken, and, with the exception of about 10 c.c., the liquid was poured into the new vessel, the exit tube of which carried a phosphorus pentoxide guard-tube.]

*First Vacuum Distillation of Main Fractions.*—The containers, holding the five main fractions from the 4-column still, were severally sealed to trains (Fig. 3) consisting of a small head-bulb A and

FIG. 3.

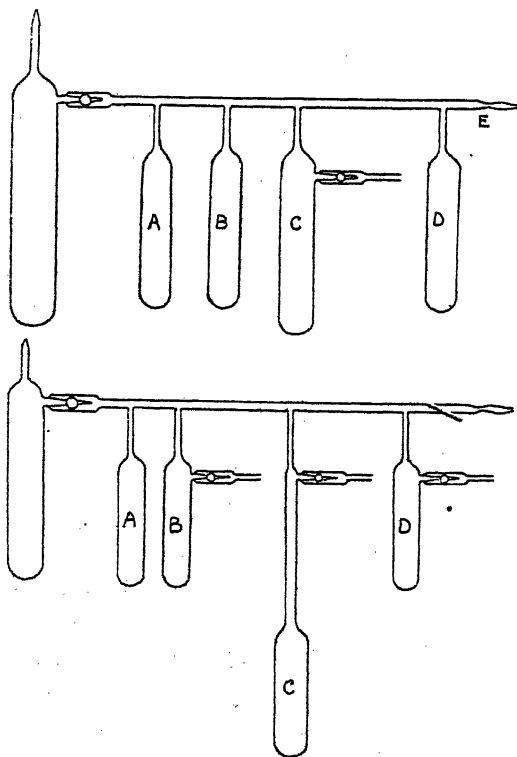
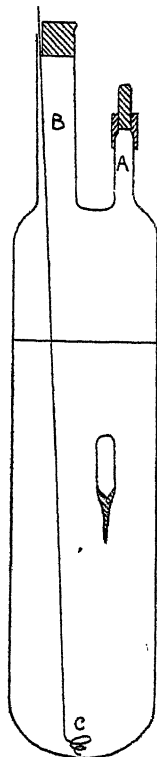


FIG. 4.

FIG. 5.



containers, B for the head fraction proper, C provided with a special joint for the main fraction, and D for the tail fraction. The train was evacuated five times while at about  $120^{\circ}$ , being each time slowly filled with dry air, and finally allowed to cool under atmospheric pressure. The silicon tetrachloride was cooled with liquid air to near its freezing point, and the capillary of the special joint was broken with the train at atmospheric pressure though still protected from moisture by the drying train. It was evacuated

and sealed off at E when the manometer registered less than 2 mm. pressure. (In the course of these distillations it was observed that solid silicon tetrachloride at very low pressures retained permanent gas which was disengaged when the solid melted.) A small head fraction of about 10 c.c. was collected in A which was sealed off, and a head fraction of 50 c.c. was distilled into B. A main fraction of about 150 c.c. was collected in C and a tail of about 50 c.c. in D, the amalgam in the original container being left quite dry.

The "hammer" of silicon tetrachloride in a vacuum at temperatures near its freezing point was considerable enough to render cautious handling absolutely necessary.

*Second Vacuum Distillation of Main Fractions.*—This was carried out after fusing to the train the main fraction containers obtained above (Fig. 4). The material was now so pure that head and tail fractions were worth preserving, and thus B and D, in addition to C, had special joints. C was specially constructed with a long neck so that it could be introduced into a water-bath, and before fusing on, into it were placed the two floats to be used subsequently in determining the density of the liquid. Very special precautions were taken in the washing and drying of the whole apparatus before the final evacuation: before the various parts were actually fitted together, each piece was treated with chromic-nitric acid for about 12 hours, well washed with tap water, then with ordinary distilled water, and finally with pure alcohol and ether and left to dry. On the day before assembling, each piece was treated with four large washings of special distilled water, followed by two with pure dry alcohol and two with pure ether. In assembling, the vessels which had to be sealed off during the course of the fractionation were held by clamps lined with asbestos paper—a provision which entirely prevented the sticking of cork and glass by repeated heating.

Each complete train was tested on the pump, and any minute leaks, which occasionally occur in such a high-melting glass as Durosil, were fused up. When finished, the apparatus was heated to about 120°, twice evacuated and slowly filled with dry air, and allowed to stand overnight protected by a new phosphorus pentoxide guard-tube. It was then evacuated six times with heating and slow refilling with dry air, the final evacuation, lasting 30 minutes, being made with the whole of the glass as near 200° as possible, and the manometer recording zero pressure when the apparatus was sealed off from the pump.

In distilling, the procedure was first to cool the whole of A with liquid air, at the same time heating C to 120°, and thus to remove any moisture from the surface of C and deposit it in A. With

these conditions still obtaining, the special joint was broken, and *instantly* a snow of solid silicon tetrachloride covered the surface of A, thus fixing any moisture and retaining it in that part of the apparatus. Further cooling was at once applied, and in about 5 minutes a small head fraction (6—9 c.c.), most of the residual air, and probably all the products of hydrolysis, if any, were removed from the system by sealing off A. This was followed by a head of about 30 c.c. in B, a main of about 60 c.c. in C, and a tail fraction of about 30 c.c. in D, leaving the original vessel dry and with the merest trace of white residue, which was greatest in the French and least in the Scottish sample. During the distillations into A and B the container C was kept warm, and the greater part of most of the distillations took place at below 0° as shown by a coating of ice on the outside of the vessels.

Before introducing them into C, the floats were gently polished with clean, well-washed linen, and a careful record was made of the destination of each float.

#### *The Preparation and Standardisation of the Floats.*

Since no method of density determination which involved exposure to air could be used with silicon tetrachloride, recourse was had to the use of glass floats. This method appeared likely to give results of much greater comparative accuracy than the older means, and actually proved to do so. It involved the preparation of two sets of floats with densities slightly above and slightly below the density of the liquid at the proposed temperature of the measurement; the determination of the relative density of these to the highest degree of accuracy attainable; and finally the observation of the flotation-temperature of pairs of these floats in the various specimens of liquid under examination. Thus, at these two temperatures the density of the liquid was known, and could be calculated very accurately at an intermediate temperature provided the interval was small. The use of two floats gave the necessary information as to the coefficient of thermal expansion of the liquid.

*Construction of Floats.*—Floats were made from thin-walled Durosil glass tubing of about 3 mm. external diameter and were of the form shown in Fig. 5. The barrel was about 12—15 mm. long, and the solid tail, which was about the same length, was in the form of a long taper. The finished floats had a smooth surface without any indentations which might serve as a place of lodgment for small bubbles. Large numbers were made and those for final adjustment were chosen by elimination. The final adjustment of the two sets was made using bromobenzene at constant temperatures

of 22.5° and 29.5°, respectively, and small amounts of glass were added to, or removed from the tails of the floats until their densities very closely approximated to that of the liquid at one of these temperatures. The magnitude of this apparently simple task will be recognised when it is remembered that 1.0° difference in flotation temperature is equivalent to about 0.001 density unit.

These bromobenzene temperatures had been chosen after comparing the flotation-temperatures of three floats in fairly pure silicon tetrachloride and then in the bromobenzene.

*Determination of the Density of the Floats.*—The density of the floats was determined by ascertaining very precisely the flotation-temperature of each float in a liquid, the density of which was afterwards determined at that particular temperature. It was realised that for the present purpose high accuracy in relative density was more important than the absolute value.

The ideal flotation-liquid would be a pure substance stable in air, non-hygroscopic, of comparatively high boiling point and having a density and a coefficient of thermal expansion about those of silicon tetrachloride. Bromobenzene approaches this ideal very closely; its density is 1.494 at 20° (Young, *Journ. de Phys.*, 1909; Perkin, J., 1896, 69, 1202); its coefficient of expansion is very near that of silicon tetrachloride, 1° change in temperature altering the densities to the extent of 0.0010 and 0.0011 unit, respectively, and its boiling point is 156° (Young, *loc. cit.*). The material first used was as supplied by The British Drug Houses, Ltd., since absolute purity seemed to be immaterial, but after it had been in use for some days a redetermination of the flotation-temperatures of three floats indicated that the liquid was changing in density (see Table IV). The liquid was therefore redistilled with the

TABLE IV.

Float.	1st Flotation-temp.*	2nd Flotation-temp.*	Difference.
C	20.735° (Oct. 30th)	20.765° (Nov. 4th)	0.030°
D	20.635       "	20.650       "	0.015
H	20.730 (Nov. 2nd)	20.758       "	0.028

\* Not corrected for exposed stem.

rejection of considerable head and tail fractions. The main fraction gave a very constant boiling point (155.4°/754.1 mm.), and if the distillate was not now chemically pure, it was at least composed of substances not readily separated by the conditions obtaining during the flotation tests. The distilled liquid was exposed to the atmosphere for 7 days, being adequately protected from dust, in order to acquire a normal moisture content. A redetermination

of the flotation-temperatures of Floats C, D, and H indicated that the density of the liquid had changed considerably (Table V).

TABLE V.

Float.	2nd Flotation-temp.*	3rd Flotation-temp.*	Difference.
C	20.765°	25.856°	5.091°
D	20.650	25.736	5.086
H	20.758	25.838	5.080

\* Not corrected for exposed stem.

On November 12th and 13th a complete set of flotation-temperatures was obtained, this being followed by the determination of the density of the liquid, and between November 17th and 20th another complete set was added. The second set showed a fall, varying between 0.007° and 0.020°, increasing with the passage of time throughout the 3 days, indicating a fall in density of the liquid which was attributed to the further absorption of moisture from the atmosphere.

The flotation-vessel was of Durosil glass in the form shown in Fig. 5, the body being about 3.5 cm. by 16 cm., and was about three-quarters filled with liquid. A was a narrow tube normally closed by a rubber cap, while B was a wider opening through which the floats were introduced and removed, and which was closed by a small cork with a groove for the passage of the float-lifter, C. This was made of No. 19 S.W.G. nichrome wire carefully cleaned and polished, and appeared to suffer no attack by the liquid. The spiral at the end served to hold the floats in a vertical position during their passage through B. The floats were handled carefully by means of nickel-plated forceps and were polished by clean, well-washed linen on entering and leaving the liquid. The wire was not lifted farther out of the liquid than was absolutely necessary and was allowed to fall back into its place after use; and, except when changing floats, B was corked and protected from dust by an inverted test-tube D. Thus every endeavour was made to ensure the permanence of the liquid during the period of the flotation-tests.

The temperature of the flotation-liquid was regulated by submerging the vessel in a tank of square cross-section holding about 27 litres of water and having large plate-glass windows at the front and back. The bath was provided with a large, mechanically-driven, propeller-shaped stirrer, an electric heater consisting of a nichrome element inside a vitreosil tube, and a cooling coil consisting of several turns of  $\frac{3}{8}$ -inch "compo" gas-piping connected to the ordinary water supply which, at the particular season of the year in question, was cold enough.

The thermometers used were: (a) Thermometer 1—a special open-scale thermometer reading from  $+9.5^{\circ}$  to  $+25^{\circ}$ , graduated in  $0.02^{\circ}$  and easily read to  $0.005^{\circ}$ ; (b) Beckmann I; (c) Beckmann II. In use, the bulb of each thermometer was about 8 inches below the surface of the water and the portion remaining was surrounded by a jacket containing water in which was a second ordinary thermometer giving the stem temperature. The observed temperature was corrected by means of the usual formula  $s = an(T - t)$  with  $a = 0.000143$  (Thorpe, J., 1880, 37, 160). Thermometers (a) and (b) were set in definite relationship, the permanence of the setting being tested from time to time, and, finally, each of the three thermometers was carefully compared with a  $0^{\circ}$ – $50^{\circ}$  open-scale thermometer, graduated in  $0.02^{\circ}$ , and recently calibrated at the National Physical Laboratory to  $0.01^{\circ}$  at each degree. All temperatures were thus accurately converted from the various arbitrary scales into degrees Centigrade.

Two methods suggested themselves for the purpose of obtaining flotation-temperatures: (a) by maintaining such a temperature that the float remained balanced in the liquid for a considerable period, say 20–30 minutes; (b) by making such slight variations in temperature as would cause the floats to rise or fall, and to take the mean of the last closely-agreeing pair of readings as the flotation-temperature. As some of the temperatures were  $15^{\circ}$  above that of the air in the room, the static method presented considerable difficulties in maintaining a constant temperature and, furthermore, failed to disclose any lag between flotation-liquid and bath temperatures. The second method was, therefore, adopted and was later modified by taking the mean of a number of *rise* and *fall* temperatures, and, by a series of time-temperature readings, ascertaining the rate at which the temperature of the bath varied. No useful purpose would be served in giving in detail all the readings from which the flotation-temperatures were ultimately derived, but a general idea of the accuracy may be obtained from the fact that out of 40 flotation-temperatures, 6 were derived from values  $0.005^{\circ}$  apart, 24 from values  $0.010^{\circ}$  apart, and 9 from values  $0.015^{\circ}$  apart.

The density of the flotation-liquid (bromobenzene) was determined at  $25.655^{\circ}$ ,  $25.666^{\circ}$ ,  $33.213^{\circ}$ , and  $33.210^{\circ}$ , the same pyknometers and method of filling being used as already described in a recent publication (Briscoe, Robinson, and Stephenson, *loc. cit.*), and only the special precautions taken to secure accuracy need be mentioned here. The pyknometer was weighed against a tare with calibrated weights on a No. 7 S.W. Oertling balance with a sensitivity of 21 divisions per mg. The vacuum weight of the



pyknometer was calculated from three separate weighings before, during, and at the conclusion of the determination, and its absolute volume was obtained by duplicate water-fillings at the two temperatures and the use of the value for the specific volume of water (Kaye and Laby, "Physical and Chemical Constants," 1911, p. 22). The liquids were delivered into the pyknometer at as near the correct temperature as possible; then the vessel was held in the bath at about  $0.10^\circ$  below the required temperature for upwards of 30 minutes, after which heat was gently applied and the temperature maintained for about 5 minutes at  $0.01^\circ$  below and then finally raised to the required temperature. In order to eliminate both speculation and observational error the temperature at the latest stage was taken at half-minute intervals and when it had remained fixed for about 4 minutes the setting was made. These temperatures were probably less than  $\pm 0.001^\circ$  in error and their accuracy was far beyond that justified by the precision of the pyknometer setting. The densities (g. per c.c.) of the flotation liquid are in Table VI, where some corresponding values by Perkin (J., 1896, 69, 1202) are given for comparison.

TABLE VI.

<i>t.</i>	<i>d.</i>	<i>d</i> (Perkin).	
25.665°	1.48766	25°/25°	1.4886
33.210	1.47741	30°/30°	1.4841
		35°/35°	1.4798

The flotation-temperatures (corrected for exposed stem) determined before and after the density work are in columns 2 and 3 respectively of Table VII, while in column 4 are the absolute flotation-temperatures derived from column 2 by the application of the calibration correction. The densities of the floats (in g. per c.c.) calculated by assuming a straight-line relationship between density and temperature over the  $7.6^\circ$  range are in column 5.

TABLE VII.

Float.	2nd Flotation-temp.	3rd Flotation-temp.	Absolute Flotation-temp.	<i>d.</i>
D	25.751°	25.736°	25.746°	1.487550
A	25.855	25.848	25.850	1.487407
E	25.849	25.841	25.844	1.487416
H	25.851	25.838	25.846	1.487413
C	25.866	25.858	25.861	1.487393
Q	32.933	32.915	32.950	1.477734
M	32.943	32.933	32.960	1.477721
L	33.013	33.003	33.028	1.477628
K	33.063	33.043	33.082	1.477554
I	33.073	33.048	33.092	1.477541

x x\* 2

*The Density of the Five Samples of Pure Silicon Tetrachloride at 20°.*

The flotation-temperatures of the two floats in the various samples gave data for the calculation of the densities of the liquids at 20.000° and their coefficients of expansion over the range 17.1° to 21.7°. In this case again a straight-line relationship was assumed over the 4.6° range.

The peculiar behaviour of the floats in silicon tetrachloride calls for comment, if for no other reason, because of the trouble it gave. The main fractions were removed from the fractionating train almost entirely in the solid condition; on the solid melting, the released floats came to the surface, and when the liquid attained room temperature (18—20°) one in each case went slowly to the bottom: in brief, the floats moved quite normally in the liquid, but with a greater velocity than in the bromobenzene for an equal temperature change on account of difference in viscosity. It was found, however, that movement of the liquid in the vessel, by shaking or even by the tremor set up by a small motor running on the same bench, caused each float to assume a positive electrical charge. These charges have not yet been completely investigated, but they were sufficient at the time to cause the floats to stick so firmly to the side of the vessel that only the most violent shaking could dislodge them, and then only for the moment, for, once released, they immediately stuck fast elsewhere. The charges gradually decreased in magnitude with the passage of time, but they were easily acquired again and evidence up to the present appears to indicate that they are not lost completely after a period of several weeks, though they may be so small as not to affect the movement of the floats.

*The Flotation-Temperatures in Silicon Tetrachloride.*—To avoid any tremor in the liquid the water-bath was fitted up in a room reserved for the purpose: the permanent, wall-side bench carried the bath, with stirrer, etc., while in front of this bench, but not touching it, was a small, absolutely steady, heavy table on which was the retort-stand carrying the container, the body of which was submerged 1.5 to 2 inches below the surface of the water. It was found that when the floats had very little charge they left the side or bottom with extreme readiness when the density was reached, and that once in the centre they could be made to go up and down several times without touching the side, surface, or bottom. When the charge was slightly greater, the floats could be dislodged by giving the retort-stand a smart tap, and when once moving even these floats could be made to go up and down several times before attaching themselves to the sides again. When the behaviour of the floats was worse than this, the container was

removed from the bath and allowed to stand for several days without disturbance. In all, 105 rising and falling temperatures were taken on the ten floats, and concordant repetitions had to be obtained before the values were accepted, but this checking, whilst it ensured absolute satisfaction, was in reality hardly necessary, for, invariably, once a float was moving freely it gave concordant results, whereas the presence of a charge too great to allow of proper freedom was immediately evident. It is probable that these flotation-temperatures in spite of the above difficulty were, by reason of increased experience and the reduced viscosity of the liquid, more accurate than the earlier ones taken in bromobenzene. Table VIII gives these flotation-temperatures in respect of each float, the corresponding density of the liquid at that temperature, and the calculated density at 20·000°.

TABLE VIII.

Source.	Float.	Flotation-temp.	$d$ at flotation-temp.	$d$ at 20°.
Canada .....	{ E	17·044°	1·487416 }	1·481231
	{ K	21·757	1·477554 }	
U.S.A. ....	{ D	16·969	1·487550 }	1·481230
	{ M	21·683	1·477721 }	
Sweden .....	{ C	17·046	1·487393 }	1·481223
	{ I	21·763	1·477541 }	
Scotland .....	{ H	17·046	1·487413 }	1·481266
	{ L	21·748	1·477628 }	
France .....	{ A	17·062	1·487407 }	1·481273
	{ Q	21·695	1·477734 }	

### Discussion of Results.

*The Densities.*—The densities of silicon tetrachloride above have an extreme variation of 0·000050, and have a mean value of 1·481245. A careful review of the method leads to the belief that these densities have a relative accuracy greater than  $\pm 0·000005$ , but their absolute value is more difficult to assess because it is based on the densities of bromobenzene, and these may possibly deviate as much as  $\pm 0·0002$  from the truth but probably not more than this. Unless the errors in the densities of bromobenzene at the upper and lower temperatures respectively are both in the same direction, their effect will be reduced in the process of computation and the absolute density of the floats is likely to be less than  $\pm 0·0002$  in error, whilst in the same way the calculation used to arrive at the density of the silicon tetrachloride probably further diminishes the error here. Thus the density of silicon tetrachloride under the pressure of its own vapour (*i.e.*, 21 mm., Becker and Meyer, *loc. cit.*; Regnault, *Mem. Acad.*, 1826, 26, 476) at 20·000°  $\pm 0·0005^\circ$  is 1·481245  $\pm 0·00005$ . This figure bears little

relationship to the previous results given below, and the reasonable presumption is that the material used by these workers was of doubtful purity.

Koster, <i>Jahresber.</i> , 1826, 6, 120 .....	1.54
Pierre, <i>Ann. Chim. Phys.</i> , 1847, 20, 27 .....	1.52371 at 0°
Mendeléeff, <i>Compt. rend.</i> , 1860, 51, 96 .....	1.4928 at 15°
Friedel and Crafts, <i>Ann. Chim. Phys.</i> , 1866, 9, 5 .....	1.522
Haagen, <i>Pogg. Ann.</i> , 1867, 131, 122 .....	1.4878 at 20°
Thorpe, <i>Ber.</i> , 1876, 9, 509 .....	1.52408 at 4°
Abati, <i>Gazzetta</i> , 1897, 27, 437 .....	1.47556 at 22°
Stiefelbogen, <i>Dispersion Flüssiger Trichloride und Tetrachloride für ultraviolette Strahlen</i> , Berlin, 1905 .....	1.524 at 16°
Ruff and Albert, <i>Ber.</i> , 1905, 38, 53, 2222 .....	1.4933 at 15°

*The Coefficients of Thermal Expansion.*—The figures given in Table VIII may obviously be used to calculate the coefficient of thermal expansion of the liquid. There seems to be no *a priori* reason for supposing that a slight difference in the isotope ratio should have any effect on this physical constant; furthermore, this constant is in a measure independent of the density determination, depending as it does upon the temperature interval only and not upon the actual readings giving the interval, and it should therefore afford an excellent check upon the soundness of the method. These coefficients of thermal expansion are given in Table IX, in which, for ease of comparison, the densities also are recorded. The former have an extreme variation of 0.0000080, and a mean value of

TABLE IX.

Source.	Density.	Diff. from mean.	Coeff. of expansion.	Diff. from mean.
Canada .....	1.481231	-0.000014	0.0014163	+0.0000039
U.S.A. ....	1.481230	-0.000015	0.0014109	-0.0000015
Sweden .....	1.481223	-0.000022	0.0014136	+0.0000012
Scotland .....	1.481266	+0.000021	0.0014083	-0.0000041
France.....	1.481273	+0.000028	0.0014129	+0.0000005
Mean .....	1.481245	±0.000020	0.0014124	±0.0000022

0.0014124, which has an error probably less than  $\pm 0.0000022$ . This figure is decidedly lower than the previous determinations, 0.001430, due to Pierre (*Ann. Chim. Phys.*, 1851, 33, 241), and 0.001446, due to Thorpe (*Proc. Roy. Soc.*, 1876, 24, 283). Without criticising the methods of the earlier workers, it will suffice to examine briefly the basis of the present determinations, *viz.*, the density and temperature intervals. The density interval depends on the densities of bromobenzene at the two temperatures: the greater the density difference the greater the coefficient of expansion indicated. Reference to p. 1277 will show that the difference in density for the given interval of temperature, 7.545°, is 0.01025 unit, whilst Perkin (*loc. cit.*) found for 10° a difference of only

0.0088 unit. Thus if Perkin's densities had been used the resulting coefficients would have been still lower. Enough has been said about flotation-temperatures to make it clear that considerable confidence may be placed in results based on them. The concordance shown by the results lends additional weight to the suggestion that they should be accepted with complete rejection of the previous data.

As criteria of the accuracy of the densities it is important to note that considerable departure from the mean seems to alternate between density and expansion in each case except in the sample from Scotland. The sample from Sweden shows the best figures. The table indicates that the causes producing the deviations are acting fortuitously, and that the errors are evenly and accidentally distributed. Thus a consideration of either column increases confidence in the other.

*The Relative Atomic Weights.*—Taking 1.481245, the mean density of the various samples, as equivalent to  $\text{Si} = 28.060$ , the atomic weights corresponding to the various densities found are set out in Table X.

TABLE X.

Origin.	Density.	At. wt.	Origin.	Density.	At. wt.
Canada .....	1.481231	28.059	Scotland .....	1.481266	28.062
U.S.A. ....	1.481230	28.059	France .....	1.481273	28.063
Sweden .....	1.481223	28.053	Mean .....	1.481245	28.060

Assuming the relative accuracy of the densities given above, these are capable of indicating changes in the atomic weight of the order of 0.001 unit, and it may reasonably be asked whether they are actually doing so here. The high value found for the French sample may perhaps be explained by the cracking of the container (see p. 1270)—a view which gains support from the observation subsequently made (see p. 1273) that this sample yielded the greatest trace of residue in the second vacuum distillation. Nothing is known against the sample from Scotland, but the considerable deviation of the coefficient of thermal expansion from the mean is probably not without significance. The evidence indicates that no greater variation than 0.005 unit in the atomic weight is to be expected in the samples of silicon under consideration.

*The Use of Floats Generally.*—It has been shown that carefully calibrated floats are capable of giving densities of liquids to a very high degree of accuracy, but it is also clear that the method could be greatly refined now that a knowledge of the technique has been obtained. To just what limit the method could be extended is not yet known. It has the advantage, however, of being applicable to any liquid which does not attack glass or silica, and may

be used to determine the coefficients of expansion and compressibility, and to follow the changes in liquids undergoing treatment in closed vessels.

The authors wish to express their deep indebtedness to Professor Briscoe for the facilities he has afforded and the interest he has constantly taken in this investigation; and they desire to acknowledge a grant from the Department of Scientific and Industrial Research which has enabled one of them (H. C. S.) to take part in this work. They have also to thank Capt. F. P. Mills, of the Northumberland and Durham Rescue Brigade, for kindly supplying the necessary liquid air.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,

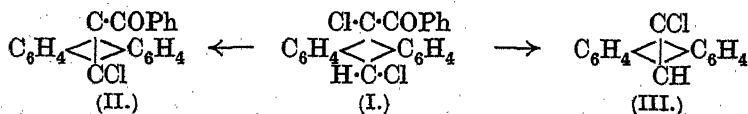
NEWCASTLE-UPON-TYNE.

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## CLXV.—*The Reactivity of meso-Substituted Anthracenes. Part I.*

By JAMES WILFRED COOK.

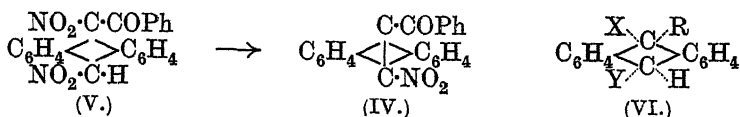
It has already been shown (Barnett, Cook, and Grainger, J., 1922, 121, 2060; Barnett, Cook, and Matthews, J., 1923, 123, 1997; Barnett and Cook, J., 1923, 123, 2631; 1924, 125, 1084; Barnett, J., 1925, 127, 2040) that in many cases *meso*-substituents in the anthracene ring system render compounds formed by addition to the "bridge" unstable or incapable of existence. The investigation of 9-benzoylanthracene (anthraphenone) has now shown that the presence of the benzoyl group hinders the formation of additive compounds. Thus with bromine no additive compound could be obtained, the sole product being 10-bromoanthraphenone. With chlorine, a similar result was obtained, although in one instance an additive compound (I) was isolated which, slowly at the ordinary temperature and rapidly on heating, lost both hydrogen chloride and benzoyl chloride and passed into a mixture of 10-chloroanthraphenone (II) and 9-chloroanthracene (III):



This behaviour suggests that the additive compound had the *trans*-configuration, but unfortunately all attempts to repeat the preparation failed, the sole product being 10-chloroanthraphenone.

The action of nitric acid on anthraphenone leads to 10-nitro-

anthraphenone (IV) (compare Lippmann and Keppich, *Ber.*, 1900, **33**, 3086), no additive compound being isolated, but with nitrogen dioxide addition takes place easily and leads to a moderately stable dinitro-compound (V) which readily loses nitrous acid under the influence of cold pyridine and passes into 10-nitroanthraphenone :



The "negative" or unsaturated benzoyl group thus resembles other negative groups in its ability to render *meso*-additive compounds unstable, and this behaviour is in general harmony with the idea of valency developed by Werner. Thus an unsaturated group at position 9 will appropriate some of the free affinity of that carbon atom; the carbon atom at 10 will accordingly have relatively more free affinity, encouraging substitution by addition at 10 rather than by addition to the "bridge." In derivatives of 9:10-dihydroanthracene (VI) the union of each *meso*-carbon atom with two unsaturated benzene nuclei results in a comparatively small amount of affinity being available for holding the other groups. These groups are thus endowed with considerable free affinity and are consequently very reactive. Thus, direct bromination of dihydroanthracene takes place with great ease, and in anthracene dibromide (R = H; X = Y = Br) the bromine atoms are very much more reactive than in a simple aliphatic bromo-compound. The tenacity with which X is held should be decreased by increasing the unsaturated nature of R, since unsaturation in R will lead to this group appropriating more affinity and hence leaving less available for holding X. A phenyl group is more unsaturated in nature than a benzoyl group (Werner, *Ber.*, 1906, **39**, 1278), so that phenylanthracene should give less stable additive compounds than benzoylanthracene. This is in accordance with fact, since, as already stated, benzoylanthracene gives an additive compound with nitrogen dioxide, whereas phenylanthracene does not (Barnett, *loc. cit.*). On the basis of the above argument the more saturated benzylanthracene should show greater capacity for undergoing additive reactions and should yield more stable additive compounds. That this is the case will be shown in a future communication.

The nature of the group R is not, of course, the only factor which influences the stability of these additive compounds. The influence of their geometrical configuration has been shown in the case of the two stereoisomeric 1:5-dichloro-9:10-dihydroanthraquinols (Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1925, **44**, 729) and

the ease with which re-establishment of the "bridge" takes place must also be affected by the affinity which the groups at 9 have for the groups at position 10.

The acyl group in the *meso*-ketones of the anthracene series is less firmly held than is usually the case with aromatic ketones. Thus anthraphenone and its chloro- and bromo-derivatives are completely hydrolysed by brief boiling with sulphuric acid in acetic acid (compare Krollpfeiffer, *Ber.*, 1923, **56**, 2360) and anthroylbenzoic acid exhibits similar instability (Heller, *ibid.*, 1921, **54**, 3627). It has already been shown (Barnett, Cook, and Matthews, *loc. cit.*) that the facile hydrolysis of anthranyl ethers is due to primary addition to the "bridge," and the hydrolysis of the ketones may be due to a similar cause, but rigorous proof is lacking. The fact that hydrogen bromide is liberated during the hydrolysis of bromoanthraphenone cannot be cited as an argument, as 9-bromoanthracene behaves in the same way under similar experimental conditions. This view of the mechanism receives support from the observation that 10-nitroanthraphenone, 10-benzoylanthraphenone and 9:10-dihydroanthraphenone are not hydrolysed by boiling with sulphuric acid in acetic acid. In the first two cases the attachment of an unsaturated group at position 10 may be regarded as diminishing the free affinity of this carbon atom and thus inhibiting 9:10-addition. In the last case addition of this nature is not possible.

Neither anthraphenone nor any of its derivatives shows any signs of visible fluorescence, so that the carbonyl group is presumably a powerful bathoflore.

#### EXPERIMENTAL.

*Anthraphenone.*—The condensation of anthracene with benzoyl chloride in presence of aluminium chloride or zinc dust (Perrier, *Ber.*, 1900, **33**, 816; Lippmann and his co-workers, *ibid.*, 1899, **32**, 2249; 1900, **33**, 3086; 1901, **34**, 2766; Krollpfeiffer, *loc. cit.*) is troublesome to carry out and tarry by-products are formed. Benzoic anhydride was therefore substituted for benzoyl chloride (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1924, **46**, 1889).

To a suspension of finely ground anthracene (90 g.) in carbon disulphide (750 c.c.) was added powdered anhydrous aluminium chloride (150 g.), followed by benzoic anhydride (175 g.\*). Reaction took place with liberation of hydrogen chloride and was brought to completion by 4 hours' heating on the water-bath.

\* If only one molecule of benzoic anhydride is employed there is formed the eutectic mixture of anthraphenone and anthracene, m. p. 158°, described by Lippmann and Keppich (*loc. cit.*) and the anthracene cannot be removed by any simple treatment.



The dark aluminium compound was decomposed with water and hydrochloric acid, the carbon disulphide removed by steam distillation, and the benzoic acid extracted from the residue by treatment with sodium hydroxide solution. After drying, the brown reaction product was treated with boiling glacial acetic acid (750 c.c.). The filtered solution, on cooling, deposited crystals which, recrystallised from benzene and then from acetic acid, yielded 85 g. of pure anthraphenone, m. p. 148°. This developed a fugitive, pure blue coloration in sulphuric acid.

The residue insoluble in acetic acid was recrystallised twice from nitrobenzene (yield, 15 g.), then from pyridine and alcohol, and finally from xylene. It formed a cream-coloured, crystalline powder, m. p. 320°, and gave a purplish-red solution in sulphuric acid (Found : C, 87.0; H, 4.8; *M*, in naphthalene, 401. Calc. for 9 : 10-dibenzoylanthracene : C, 87.0; H, 4.7%; *M*, 386). Lippmann and Fleissner (*Ber.*, 1899, **32**, 2249) obtained this substance as a by-product in the preparation of anthraphenone, but in a later paper (Lippmann and Keppich, *ibid.*, 1900, **33**, 3086) the by-product was described as tribenzoylanthracene. This compound gave anthraquinone on oxidation and this and other properties of the substance indicate that it was really impure dibenzoylanthracene.

9 : 10-Dibenzoylanthracene is obtained in 20% yield when anthraphenone is treated with an excess of benzoic anhydride in presence of anhydrous aluminium chloride. The positions assigned to the benzoyl groups follow from a study of the reduction products (future communication).

**10-Bromoanthraphenone.**—A suspension of anthraphenone (2.5 g.) in carbon disulphide (15 c.c.) was cooled in a freezing mixture, and bromine (0.5 c.c.; 1 mol.), dissolved in carbon disulphide (5 c.c.), was added slowly. Hydrogen bromide was liberated and since the addition of pyridine yielded only pyridine hydrobromide and no quaternary salt it is unlikely that addition of bromine had occurred. The bromo-derivative was obtained by evaporating the solution and crystallising the residue from acetic acid, benzene, and finally ethyl acetate (Found : Br, 22.0.  $C_{21}H_{13}OBr$  requires Br, 22.2%).

**10-Bromoanthraphenone** forms pale yellow nodules, m. p. 175—176°. It gives a deep blue solution in sulphuric acid, the colour being less fugitive than in the case of anthraphenone itself. The same compound is obtained when the bromination is carried out in boiling glacial acetic acid solution. If two molecules of bromine are employed and the boiling is continued for an hour, the bromoanthraphenone is contaminated with 9 : 10-dibromoanthracene, this compound being formed by partial hydrolysis of the bromoanthraphenone and subsequent bromination.

**10-Chloroanthraphenone.**—Anthraphenone (5.6 g.) was added to a solution of chlorine in carbon tetrachloride (20 c.c.; 7.5%, wt.-vol.), the mixture boiled for 15 minutes, cooled, and light petroleum added. The resulting solid crystallised from glacial acetic acid, benzene and finally ethyl acetate in yellow nodules, m. p. 164—165° (Found : Cl, 11.3.  $C_{21}H_{13}OCl$  requires Cl, 11.2%).

**9 : 10-Dichloro-9 : 10-dihydroanthraphenone.**—A solution of anthraphenone (11.4 g.) in carbon tetrachloride (40 c.c.) was cooled in ice, chlorine in carbon tetrachloride solution (40 c.c.) added, the mixture kept in ice for 2 hours, and light petroleum added. The resulting solid crystallised from warm benzene-light petroleum in colourless needles, m. p. 110—111° (decomp.). After being kept in a vacuum desiccator for 2 days, the substance smelled strongly of benzoyl chloride, so the sample for analysis was recrystallised from benzene and light petroleum and dried in a vacuum desiccator for 3½ hours (Found : Cl, 19.8.  $C_{21}H_{14}OCl_2$  requires Cl, 20.1%).

The dichloride (0.5 g.) was suspended in cold pyridine (1 c.c.) and after an hour ether was added and the solid recrystallised from alcohol and ether. It formed colourless needles completely soluble in water, and although analysis showed that the substance was not pure it was evident that both chlorine atoms of the dichloride had suffered displacement by pyridinium groups (Found : Cl, 14.4.  $C_{31}H_{24}ON_2Cl_2$  requires Cl, 13.9%).

**Thermal Decomposition of Anthraphenone Dichloride.**—The dichloride (0.1 g.) was heated to its melting point; hydrogen chloride and benzoyl chloride (identified by its smell) were then liberated. The resulting mixture was fractionally crystallised from alcohol into (a) 10-chloroanthraphenone, identified by the method of mixed melting points, and (b) slender, yellow needles, m. p. 96—98°, which gave solutions having a strong violet fluorescence. The identification was completed by direct comparison with an authentic sample of 9-chloroanthracene.

**10-Nitroanthraphenone.**—Anthraphenone, suspended in acetic acid, was slowly nitrated by nitric acid (1 mol.;  $d$  1.42) in the cold without the production of an additive compound. The reaction was best completed by heating on the water-bath for a few minutes; the nitro-compound was then obtained pure without the elaborate purification recommended by Lippmann and Keppich (*loc. cit.*).

**9 : 10-Dinitro-9 : 10-dihydroanthraphenone.**—A stream of nitrogen dioxide (2.6 g.) prepared by heating a mixture of lead nitrate and sand, was led into a solution of anthraphenone (5.6 g.) in chloroform (10 c.c.), cooled in a freezing mixture; after an hour light petroleum was added. The resinous substance that separated became solid when ground under ether. Thrice recrystallised from chloroform

and light petroleum and dried in a vacuum desiccator, it was obtained in colourless needles, m. p.  $175^{\circ}$  (decomp.) (Found: N, 7.8.  $C_{21}H_{14}O_5N_2$  requires N, 7.5%). Suspended over-night in cold pyridine diluted with alcohol, it lost nitrous acid and passed into 10-nitroanthraphenone (identified by the method of mixed melting points).

*Fission of Anthraphenone Derivatives.*—In order to compare the influence of the substituent in the 10-position the same conditions were employed in all cases. Krollpfeiffer (*loc. cit.*) has shown that if this substituent is hydroxyl, hydrolysis can be effected by boiling with hydrochloric acid in acetic acid, whereas anthraphenone itself is unaffected under these conditions.

10-Chloro-, 10-bromo-, and 10-nitro-anthraphenone were all recovered unchanged after 4 hours' boiling with hydrochloric acid in acetic acid. Chloroanthraphenone was not affected by heating for 5 hours at  $170^{\circ}$  with acetic acid saturated with hydrogen chloride.

Hydrolysis with sulphuric acid was attempted by boiling the substance (1 g.) with acetic acid (10 c.c.) containing sulphuric acid (1 c.c.) for  $\frac{1}{2}$  hour. Krollpfeiffer's observation that anthraphenone is completely decomposed into benzoic acid and anthracene was confirmed. Bromoanthraphenone and chloroanthraphenone gave tarry products (in the former case hydrogen bromide was liberated), whilst 9:10-dihydroanthraphenone, 10-nitroanthraphenone and 9:10-dibenzoylanthracene were recovered unchanged (in the last case after 3 hours' boiling).

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this investigation, and to Dr. E. de Barry Barnett for gifts of materials.

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## CLXVI.—*The Solubility of Beryllium Oxide in Solutions of its Salts.*

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AQUEOUS solutions of beryllium salts are known to be able to dissolve considerable quantities of the oxide, a property also possessed, but in a much smaller degree, by salts of iron, aluminium, and some other metals. A concentrated solution of the beryllium

salt of a strong acid continues to dissolve the basic carbonate with brisk effervescence even after the addition of more than one mole of base to each mole of salt present.

With the sulphate, Parsons (*J. Amer. Chem. Soc.*, 1904, **26**, 1433) found that the solubility of the oxide increased with the concentration of the salt, and in strong solution exceeded two moles to one mole of salt. No definite basic salts could be isolated : on dilution the more highly basic solutions gave flocculent precipitates ; on evaporation all left glassy residues with varying ratios of  $\text{Be} : \text{SO}_4$ . The basic sulphates described by Berzelius and others were shown not to be definite compounds. Similar results were obtained with the oxalate (Parsons and Robinson, *ibid.*, 1906, **28**, 555). Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651) showed that the f. p. of beryllium sulphate solution is slightly raised by the addition of the oxide, and its conductivity slightly diminished ; they concluded that the basic solutions are not colloidal, since they cannot be separated by dialysis, and are not coagulated by electrolytes. The only suggestion they make to explain the results is that the salt solution acts as a mixed solvent, the oxide dissolving in the salt as camphor dissolves in acetic acid even when it is diluted with water.

Recently Britton (*J.*, 1925, **127**, 2121) has examined electrometrically the effect of adding sodium hydroxide to beryllium sulphate solution. He finds that no precipitation occurs until 1.04 moles of sodium hydroxide have been added for each mole of beryllium sulphate. He concludes that the solution is mainly colloidal, although he admits that it is not coagulated by electrolytes and that it " betrays no sign of colloidality."

We have examined the question by measurements of (1) the solubilities and (2) the viscosities and conductivities of these basic solutions. Parsons's investigation of the system  $\text{BeO}, \text{SO}_4, \text{H}_2\text{O}$  did not extend beyond solutions containing 5%  $\text{BeSO}_4$ , and his results were vitiated, as he admits, by the absence of any definite solid phase. The only such phase appears to be the normal sulphate  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , and we have therefore determined the effect of addition of the oxide on the solubility of this salt : similar measurements were also made with the selenate and the oxalate. As the existence of an acid oxalate has been asserted and denied, the system  $\text{BeC}_2\text{O}_4, \text{H}_2\text{C}_2\text{O}_4, \text{H}_2\text{O}$  also was examined.

In addition, the conductivities of neutral and basic chloride and oxalate solutions and the viscosities of neutral and basic chloride, oxalate, sulphate, and selenate solutions were measured.

## EXPERIMENTAL.

*Solubility of Beryllium Sulphate.*—The sulphate was purified by recrystallisation from water. The hydroxide, precipitated with ammonia, was dissolved in ammonium carbonate, precipitated as the basic carbonate by passing in a current of steam, washed, and heated for several hours in water through which a current of air was drawn.

Suitable complexes were made by dissolving this basic carbonate in concentrated solutions of the sulphate, boiling to expel carbon dioxide, and filtering. They were rotated in the thermostat at  $25.00^\circ \pm 0.05^\circ$  in rubber-stoppered tubes for periods varying from 20 hours for the more dilute to 200 hours for the most concentrated and viscous solutions, from which the salt crystallised rather slowly. For each analysis two samples were withdrawn through cotton-wool filters into calibrated pipettes, and weighed, giving approximate values of the density. One of these was evaporated to dryness with excess of sulphuric acid and weighed as  $\text{BeSO}_4$  (which is stable up to  $500^\circ$ : Kraus and Gerlach, *Z. anorg. Chem.*, 1924, **140**, 69) or heated in a muffle and weighed as  $\text{BeO}$ . In the other, the  $\text{SO}_4$  was determined with barium chloride. The moist solids obtained by filtration were analysed in the same way. The increasing viscosity made it impossible to measure the complete isotherm. The solid phase was shown by the residue method to be in all cases  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ . As the amount of dissolved beryllium oxide is obtained by difference, and also on account of its very low equivalent weight, the experimental error is necessarily large.

The results are in Table I.

TABLE I.  
Solubility of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  in presence of  $\text{BeO}$ .

$d_{25}^{25^\circ}$ .	Per cent.		Extra $\text{BeSO}_4$ .	Molecular ratio.	
	$\text{BeSO}_4$ .	$\text{BeO}$ .		$\text{BeO} : \text{BeSO}_4$ .	$\text{BeO} : \text{extra BeSO}_4$ .
1.278	29.74	—	—	—	—
1.318	31.73	2.16	1.99	0.286	4.55
1.327	32.12	2.62	2.38	0.343	4.62
—	33.86	4.03	4.12	0.500	4.11
1.347	34.55	4.26	4.81	0.517	3.75
—	34.87	5.02	5.13	0.605	4.11
—	36.46	6.10	6.72	0.703	3.81
1.416	37.48	7.73	7.74	0.867	4.19
				Mean	4.14

The solubility of the pure sulphate at  $25^\circ$  was found to be 29.74%, which agrees fairly well with the value, 29.94%, obtained by Britton and Allmand (*J.*, 1921, **119**, 1463).

In the last column is given the molecular ratio of the oxide present to the increase of solubility of the sulphate. It thus appears that 1 molecule of salt dissolves for every 4 molecules of oxide added.

In the analogous case of increasing solubility of lead acetate in the presence of lead oxide (Jackson, *J. Amer. Chem. Soc.*, 1914, **36**, 2346) the results calculated in this way show a much more rapid increase of solubility (about 3 moles of acetate to one of oxide).

To see whether the effect is general, other beryllium salts should be examined. Most of the salts, however, are excessively soluble, and many (*e.g.*, the chloride) crystallise with difficulty, especially in presence of the base. The perchlorate,  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ , was prepared, but its solubility at 25° was found to be 59.5% (anhydrous salt). The *benzenesulphonate* and the *p-toluenesulphonate*, which have not been previously described, were prepared by crystallisation from a solution of the basic carbonate in slightly more than its equivalent of the acid. These salts gave off their water of crystallisation at 100°; decomposition also commenced at that temperature. The salts were recrystallised from water. The *benzenesulphonate* formed small, elongated tablets [Found:  $\text{BeO}$ , 6.3.  $\text{Be}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$  requires  $\text{BeO}$ , 6.33%. Solubility at 25° = 53.8% (of anhydrous salt)]. The *p-toluenesulphonate* formed a mass of minute crystals which were only slightly denser than their saturated solution [Found:  $\text{BeO}$ , 5.9.  $\text{Be}(\text{C}_7\text{H}_7\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$  requires  $\text{BeO}$ , 5.91%. Solubility at 25° = 39.2% (of anhydrous salt)].

The great solubility of these three salts, and the difficulty of estimating the anions accurately, make them unsuitable: the only suitable salts seem to be the selenate and oxalate.

*Solubility of Beryllium Selenate.*—The salt was prepared by dissolving the basic carbonate in a slight excess of selenic acid, made by the oxidation of selenious acid with chloric acid (Meyer and Moldenhauer, *Z. anorg. Chem.*, 1921, **116**, 193), and was twice recrystallised from water. It was free from selenite, and had the composition  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$  (Found:  $\text{BeO}$ , 11.3; Se, 35.4;  $\text{H}_2\text{O}$ , 32.7. Calc.:  $\text{BeO}$ , 11.15; Se, 35.3;  $\text{H}_2\text{O}$ , 32.1%). The selenate was determined by reduction to selenium (Jannasch and Müller, *Ber.*, 1898, **31**, 2388). The salt loses rather more than half its water at 100–105°, and the rest at 300°, at which temperature the anhydrous salt is quite stable.

The solubilities were measured as before. The results at 25° are in Table II, each being the mean of two determinations.

The molecular ratio is the same as with the sulphate, within the limits of experimental error.

TABLE II.

Solubility of  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$  in presence of  $\text{BeO}$ .

Per cent.		Extra $\text{BeSeO}_4$ .	Molecular ratio.	
$\text{BeSeO}_4$ .	$\text{BeO}$ .		$\text{BeO} : \text{BeSeO}_4$ .	$\text{BeO} : \text{extra BeSeO}_4$ .
36.22	0.046	—	0.008	—
37.05	0.60	0.83	0.098	4.0
38.84	1.98	2.62	0.311	4.5
40.23	2.98	4.01	0.451	4.4
42.11	3.71	5.89	0.536	3.8
				Mean 4.2

*Solubility of Beryllium Oxalate.*—The salt was prepared from the basic carbonate and slightly more than its equivalent of oxalic acid and the measurements were carried out in the same way as before. Parsons and Robinson (*loc. cit.*) state that the slightest excess of base entirely prevents the crystallisation of the oxalate. This was not confirmed, although the crystallisation from the more basic solutions is rather slow, lasting about a day.

The results at  $25^\circ$  are in Table III.

TABLE III.

Solubility of  $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  in presence of  $\text{BeO}$ .

$d_{4}^{25}$ .	Per cent.		Extra $\text{BeC}_2\text{O}_4$ .	Molecular ratio.	
	$\text{BeC}_2\text{O}_4$ .	$\text{BeO}$ .		$\text{BeO} : \text{BeC}_2\text{O}_4$ .	$\text{BeO} : \text{extra BeC}_2\text{O}_4$ .
1.179	28.20	0.08	—	0.011	—
1.224	31.73	1.31	3.53	0.160	1.35
1.259	35.01	2.35	6.81	0.260	1.29
1.282	37.17	3.23	8.97	0.337	1.36
—	41.69	4.02	13.49	0.373	(1.13)
1.290	38.20	3.52	10.00	0.367	1.33
				Mean 1.33	

The analysis of the moist solids from experiments 2, 3, and 4 showed the solid phase to be in each case the normal oxalate  $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ . In calculating the results in the last column, the small quantity of oxide present in the first experiment was subtracted. The calculated solubility of the pure oxalate at  $25^\circ$  is 27.97%.

The oxalate thus resembles the sulphate and selenate in that its solubility is increased by the addition of the oxide, but the rate of increase is three times as great: 3 molecules of salt for every 4 molecules of oxide added.

In view of the possible formation of complex oxalates, the system was examined on the acid side ( $\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ). Rosenheim and Woge (*Z. anorg. Chem.*, 1897, **15**, 283) obtained from a solution containing excess of oxalic acid crystals of the composition

$2\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ . Parsons and Robinson (*loc. cit.*) could not obtain this, but only mixtures of crystals which were recognised under the microscope as those of the normal oxalate and of oxalic acid; they observed that the last traces of oxalic acid were very difficult to remove from the salt by recrystallisation. Wirth (*Z. anorg. Chem.*, 1914, **87**, 7) found the solubility of  $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  in water at  $25^\circ$  to be 24.85% (of anhydrous salt), and in *N*/10-oxalic acid 27.75%, from which he concludes that complex acid salts are formed. The former value does not agree with our results, but the latter does, our values for the corresponding solubilities being 27.8% and 27.5%, respectively.

The system  $\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  was measured at  $25^\circ$  by the methods already described. The complexes were heated until homogeneous, and rotated 18–36 hours in the thermostat to crystallise. The results are in Table IV. Compositions are in weights %.

TABLE IV.  
System  $\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  at  $25^\circ$ .

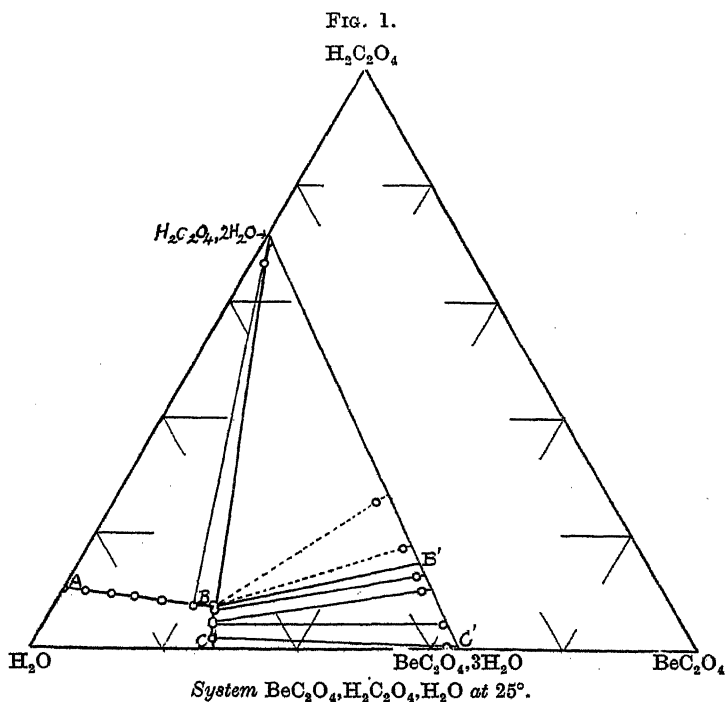
No.	$d_{4^\circ}^{25^\circ}$ .	Percentage composition.			
		Solution.		Moist solid.	
		$\text{BeC}_2\text{O}_4$ .	$\text{H}_2\text{C}_2\text{O}_4$ .	$\text{BeC}_2\text{O}_4$ .	$\text{H}_2\text{C}_2\text{O}_4$ .
1	1.178	26.55	1.81	62.18	0.45
2	1.187	25.33	4.42	59.85	4.40
3	1.188	25.23	4.79	53.57	10.11
4	1.197	24.49	6.88	51.53	12.68
5	1.184	23.90	7.51	47.15	17.60
6	1.197	24.01	7.46	39.11	25.38
7	1.168	20.78	7.63	1.90	66.76
8	1.139	15.79	8.46	—	—
9	1.112	11.24	9.07	—	—
10	1.087	7.60	9.52	—	—
11	1.064	3.45	10.03	—	—
12	1.043	0.00	10.23	—	—

The results are plotted in Fig. 1. The curve AB gives solutions in equilibrium with  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ; curve BC those in equilibrium with solids ranging from B' to C' which are obviously mixed crystals of  $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . It will thus be seen that there is no evidence for the existence of an acid salt such as that described by Rosenheim and Woge. This mixed crystal formation also explains the difficulty of Parsons and Robinson in removing the last of the oxalic acid impurity from beryllium oxalate by recrystallisation. It is very unusual for a salt to form mixed crystals with its own acid.

*Measurement of Viscosities.*—Concentrated solutions of the sulphate and the selenate were made up from the crystalline salts; those of the chloride and oxalate by dissolving the basic carbonate



in the necessary amount of acid, and determining the composition by analysis. The basic solutions, likewise analysed, were made up in the same way. They were all carefully filtered, and the dilute solutions made up from them by weight. The densities were measured in a pycnometer, and the viscosities in an Ostwald viscometer of period 84.6 seconds with water at 25°. Every value is the mean of two or more concordant results. The values given in Tables V and VI are of the equivalent normality of the salt, and of the relative viscosity (water at 25° = 1).



It will be seen that the increase of viscosity caused by the base in dilute solutions is relatively small, and is little affected by the nature or concentration of the salt. The viscosity of the solution did not change on standing, or on heating to 100° and cooling again, which indicates that the phenomenon is not colloidal.

*Conductivities.*—These were measured in the usual way for neutral and basic chloride and oxalate solutions made up and analysed as above described, the results being given in Tables VII—X. The conductivity of the water ( $1.3$  to  $1.9 \times 10^{-6}$ ) was subtracted. The concentrations are equivalent normalities of salt present; the

TABLE V.

Viscosities of neutral and basic solutions of beryllium chloride.

Equivalent normality.	$\eta_{25}^{25}$	Relative viscosity (water at 25° = 1).	Composition of solution.
0.338	(1.0089)	1.076	Neutral (equivalents Be : Cl = 0.997 : 1.000).
0.683	(1.0178)	1.170	
1.014	1.0265	1.245	
1.936	1.0494	1.524	
2.770	1.0700	1.816	
3.810	1.0948	2.255	
5.308	1.1295	3.065	
7.671	1.1852	5.184	
0.569	1.0182	1.153	Basic (0.476 mole BeO per mole BeCl <sub>2</sub> ).
1.209	1.0394	1.355	
2.255	1.0721	1.761	
3.274	1.1009	2.299	
4.757	1.1437	3.485	
5.990	1.1780	4.943	
7.539	1.2242	8.005	
0.590	(1.0223)	1.192	Basic (0.987 mole BeO per mole BeCl <sub>2</sub> ).
0.899	(1.0339)	1.295	
1.741	(1.065)	1.653	
2.460	1.0902	2.056	
3.602	1.1311	2.970	
4.633	1.1662	4.299	
4.955	1.1762	4.836	
6.028	1.2110	7.322	
7.350	1.2550	13.36	
0.0472	1.0022	1.016	Basic (1.760 moles BeO per mole BeCl <sub>2</sub> ).
0.1080	1.0050	1.036	
0.340	1.0160	1.114	
0.641	1.0301	1.238	
1.055	1.0489	1.441	
1.738	1.0792	1.893	
4.190	1.1855	6.968	

conductivities are also equivalent. The fourth column gives the product of the conductivity and the viscosity. Temperature  $25^\circ \pm 0.02^\circ$ . The values for the chloride solutions are in Tables VII and VIII ( $b$  = moles of BeO per mole of salt).

In Fig. 2, the product of equivalent conductivity and viscosity is plotted against the cube root of the concentration, the crosses representing the values of Fricke and Schützdecker (*Z. anorg. Chem.*, 1924, 131, 130) for solutions obtained by double decomposition from beryllium sulphate and barium chloride. It will be seen that the conductivity is less in the basic solutions, but only by about 5%.

The hydrogen-ion concentration in beryllium chloride solutions at  $25^\circ$  has been measured colorimetrically by Mr. W. J. Worboys in this laboratory (results not yet published). He finds this to vary from 1.24% of the salt concentration in  $N/8$ -solution to 3.68% in  $N/512$ . If we assume that the hydrolysis takes place thus:  $\text{BeCl}_2 + \text{H}_2\text{O} = (\text{BeOH})\text{Cl} + \text{HCl}$ , the practical result will be to

TABLE VI.

Viscosities of neutral and basic solutions of beryllium salts.

Equivalent normality.	$\alpha_{25}^{25}$ .	Relative viscosity (water at 25° = 1).	Solution.
0.425	(1.019)	1.147	Beryllium sulphate (neutral).
0.644	1.0290	1.221	
1.109	1.0503	1.420	
1.737	1.0782	1.730	
2.638	1.1163	2.312	
3.874	1.1663	3.644	
5.878	1.2454	7.199	
0.455	1.0254	1.189	Beryllium sulphate basic (0.965 mole BeO per mole BeSO <sub>4</sub> ).
0.666	1.0367	1.292	
1.078	1.0593	1.516	
1.654	1.0900	1.926	
2.382	1.1274	2.644	
3.319	1.1747	4.069	
4.022	1.2104	5.843	
5.045	1.2601	10.20	
6.432	1.3240	22.80	
7.702	1.3783	51.1	
8.933	(1.426)	140.6	
0.457	1.0297	1.167	Beryllium selenate (neutral).
0.981	1.0634	1.386	
2.027	1.1288	1.985	
3.111	1.1950	2.903	
4.771	1.2940	5.864	
0.483	1.0373	1.215	Beryllium selenate basic (0.979 mole BeO per mole BeSeO <sub>4</sub> ).
0.983	1.0761	1.508	
2.130	1.1624	2.569	
3.336	1.2464	4.599	
4.737	1.3429	11.00	
0.565	1.0160	1.098	Beryllium oxalate neutral (equivalents Be : C <sub>2</sub> O <sub>4</sub> = 0.996 : 1.000).
1.138	1.0325	1.207	
2.324	1.0663	1.493	
3.671	1.1047	1.950	
4.971	1.1419	2.564	
0.556	1.0230	1.156	Beryllium oxalate (0.974 mole BeO per mole BeC <sub>2</sub> O <sub>4</sub> ).
1.085	1.0439	1.329	
2.267	1.0896	1.909	
3.569	1.1426	3.058	
5.011	1.1980	5.757	

TABLE VII.

Conductivities of beryllium chloride (neutral) solutions.

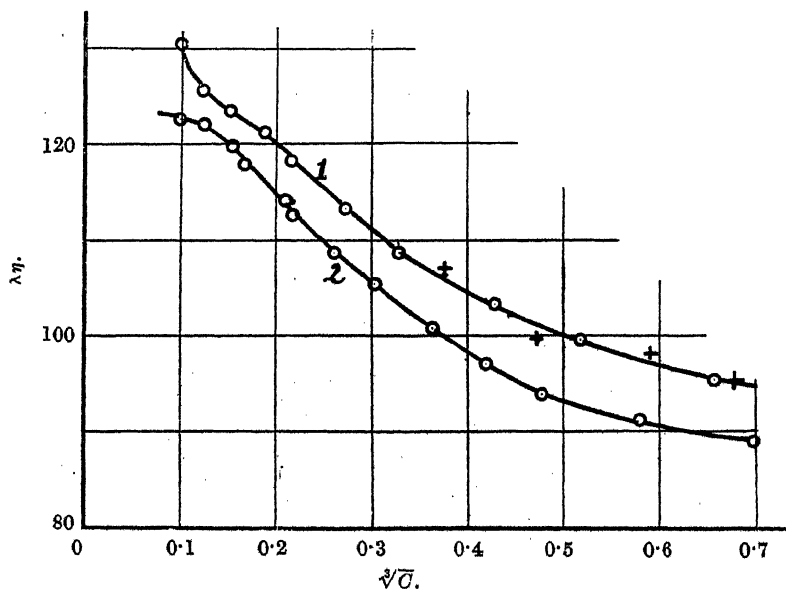
Normality.	Relative viscosity ( $\eta$ ).	Equivalent conductivity ( $\lambda$ ).	$\lambda\eta$ .	$\lambda\eta$ (corr.).
0.001001	—	130.6	130.6	115.8
0.001832	—	125.8	125.8	114.1
0.003467	(1.001)	123.4	123.5	113.7
0.006491	(1.002)	121.1	121.3	113.3
0.009964	(1.002)	118.2	118.4	111.3
0.02014	(1.005)	112.8	113.3	107.5
0.03392	(1.008)	108.1	108.9	103.9
0.07863	(1.019)	101.3	103.3	98.8
0.1387	(1.034)	96.5	99.8	95.7
0.2840	(1.069)	89.4	95.6	—
0.5548	(1.136)	81.1	92.1	—
1.0140	1.245	72.1	89.8	—

TABLE VIII.

Conductivities of beryllium chloride (basic,  $b = 1.760$ ) solutions.

Normality.	$\eta$ .	$\lambda$ .	$\lambda\eta$ .	Normality.	$\eta$ .	$\lambda$ .	$\lambda\eta$ .
0.000967	—	122.9	122.9	0.04724	1.016	99.3	100.9
0.000972	—	122.8	122.8	0.07257	(1.025)	94.9	97.2
0.001850	—	122.2	122.2	0.1164	(1.039)	90.5	94.0
0.003568	(1.001)	119.9	120.0	0.1968	(1.066)	85.6	91.3
0.004637	(1.002)	117.8	118.0	0.3400	1.114	80.0	89.1
0.009196	(1.003)	113.7	114.0	0.6415	1.238	71.4	88.4
0.01015	(1.003)	112.3	112.6	1.0546	1.441	63.1	91.0
0.01763	(1.006)	107.9	108.6	1.738	1.893	52.7	99.9
0.02725	(1.009)	104.4	105.3	4.190	6.968	26.93	187.7

FIG. 2.



Equivalent conductivities of beryllium chloride solutions. Curve 1, neutral solution  
Curve 2, basic ( $b = 1.760$ ) solution.

+ denotes observations by Fricke & Schützdelier (*loc. cit.*).

increase the conductivity by an amount corresponding to the hydrogen ion present. By subtracting this amount we find the conductivity of the non-hydrolysed solutions (last column in Table VII). As will be seen, this correction brings the values of the neutral very near to those of the basic solutions, except at high dilutions, where even the latter may still be perceptibly hydrolysed.

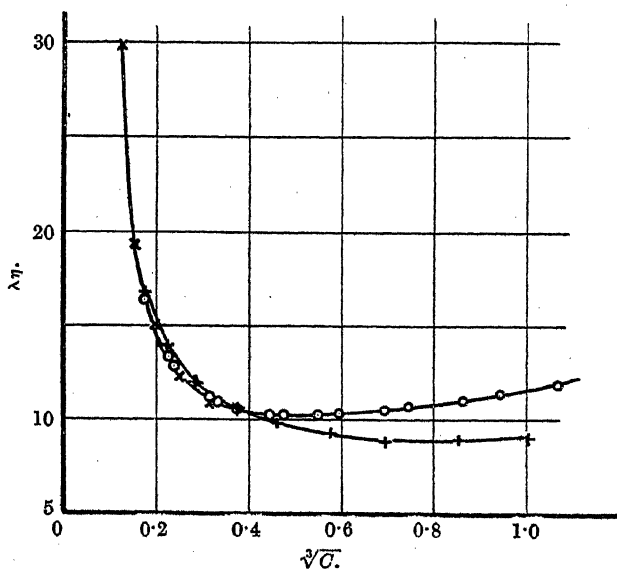
The corrected conductivities of the solutions of the neutral chloride extrapolate to a value for the mobility at  $25^\circ$  of  $\frac{1}{2}\text{BeCl}_2 = 118.5$ , corresponding to 43 for  $\frac{1}{2}\text{Be}$ . Fricke and Schützdelier (*loc.*

*cit.*) give a value of 30 for the mobility of  $\frac{1}{2}\text{Be}$ . This is based on their values for the conductivities of solutions from 0.05*N* to 0.5*N*; but their correction for hydrolysis is rather uncertain, being founded on a measurement by Wood (J., 1910, 97, 878) of its value (2.2%) at 0.35*N*, from which they calculated the values at greater dilutions.

The values for the oxalate solutions are in Tables IX and X.

The results are plotted in Fig. 3, the crosses representing those of Rosenheim and Woge (*loc. cit.*).

FIG. 3.



*Equivalent conductivities of beryllium oxalate solutions.*

○ *Neutral solutions.* × *Neutral solutions (Rosenheim and Woge).* + *Basic (b = 0.974) solutions.*

TABLE IX.

Conductivities of beryllium oxalate (neutral) solutions.

Normality.	$\eta$ .	$\lambda$ .	$\lambda\eta$ .	Normality.	$\eta$ .	$\lambda$ .	$\lambda\eta$ .
0.00550	1.001	16.38	16.39	0.1657	1.028	9.95	10.22
0.01407	1.002	12.81	12.83	0.2136	1.036	9.97	10.32
0.01180	1.002	13.32	13.35	0.3351	1.057	9.95	10.51
0.03202	1.005	11.08	11.13	0.4164	1.072	9.99	10.71
0.03732	1.006	10.87	10.93	0.6478	1.115	9.87	11.00
0.05323	1.009	10.49	10.58	0.8372	1.149	9.94	11.42
0.08931	1.015	10.12	10.27	1.1403	1.209	9.67	11.69
0.1084	1.019	10.09	10.28				

TABLE X.

Conductivities of beryllium oxalate (basic,  $b = 0.974$ ) solutions.

Normality.	$\eta$ .	$\lambda$ .	$\lambda\eta$ .	Normality.	$\eta$ .	$\lambda$ .	$\lambda\eta$ .
0.00574	1.001	16.79	16.81	0.1897	1.052	8.85	9.31
0.01144	1.003	13.93	13.98	0.3397	1.094	8.02	8.78
0.02359	1.007	11.88	11.96	0.6236	1.178	7.60	8.95
0.05392	1.015	10.35	10.51	1.0245	1.307	6.90	9.02
0.1012	1.028	9.53	9.80				

The conductivities of the oxalate are very small, as may be seen by comparing them with those of the sulphate (Ley, *Z. physikal. Chem.*, 1899, 30, 245) at the same dilutions.

Dilution (litres per equiv.) .....	32	128	512
Equiv. cond. of sulphate .....	66.4	88.7	112.6
„ „ of oxalate .....	10.8	15.1	29.8

Further, the equivalent conductivity of the oxalate solution increases at concentrations above about 0.15*N*, which behaviour is probably unprecedented.

*Freezing Points of Oxalate Solutions.*—The depression of freezing point of aqueous solutions of the oxalate was measured in a Beckmann apparatus. The results are

Mole of salt per 1000 g. of water.	$\Delta$ .	Molecular depression.	$i$ .
0.0224	0.048°	2.14°	1.15
0.0532	0.119	2.24	1.20
0.1049	0.220	2.10	1.13
0.1771	0.363	2.05	1.10
0.3665	0.720	1.96	1.05

The values of the van 't Hoff factor  $i$  are, in the stronger solutions, of the same order as those observed by Parsons, Robinson, and Fuller (*loc. cit.*), but at greater dilutions they are considerably lower.

#### *Discussion of Results.*

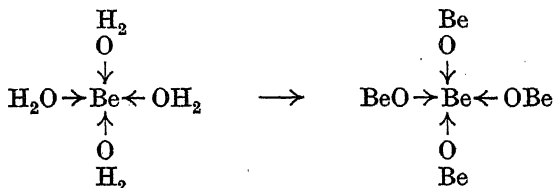
(1) *Sulphate, Selenate, and Chloride.*—The solubility of beryllium oxide in solutions of its salts may be due to three causes. (1) The salt may make the oxide form a colloidal solution; (2) the oxide may form a basic salt, for example of the univalent ion  $[\text{BeOH}]^+$ , or (3) it may attach itself to one of the ions of the normal salt, in which case, since the property is common to beryllium salts in general, it must combine with the beryllium ion. The first hypothesis, that of colloid formation, has not been entirely disproved. The most basic solutions are somewhat turbid, and although they cannot be separated by dialysis, they may contain some colloidal material. But the whole of the dissolved oxide cannot be in this form. Some of the solutions described above contain more than 2, and they can be prepared with as many as 5 moles of oxide per

litre, a concentration enormously greater than is reached by the colloidal solutions of other metallic hydroxides. Further, the stability of these solutions to the action of heat and of electrolytes is against the view that they are highly concentrated colloids, a view which also fails to explain why the salt is more soluble in presence of the oxide. The bulk of the oxide must be present in some other form. (2) The formation of basic salts of an ion  $[\text{BeOH}]^+$  would not allow of the solution of more than one mole of oxide for every mole of salt, whereas more basic solutions can be prepared. It would also involve an increase of one ion for every molecule of oxide dissolved— $[\text{Be}]A + \text{Be}(\text{OH})_2 = [\text{BeOH}]_2A$ —and hence the addition of oxide should lower the freezing point and probably increase the conductivity, whereas it actually has the opposite effect.

We are therefore left with the third hypothesis, that the oxide combines with the beryllium ion to form a complex kation  $[\text{Be}_x\text{BeO}]^{++}$ . This would account for the small change in conductivity (3—7%, mainly due to the disappearance of hydrolysis), since the number of ions would not alter, but the "beryllated" ion might have a slightly different mobility and degree of ionisation. It is also supported by the slight decrease (about 10%) in the freezing point depression of the sulphate observed by Parsons, Robinson, and Fuller (*loc. cit.*). It explains the increase in the solubility of the salt in presence of the oxide as due to the formation of a new complex salt. If we could assume the solubility of the normal salt to be the same in presence of the complex salt as in water, the molecular ratio of the added oxide to the increased solubility of the salt (4.14 with the sulphate and 4.2 with the selenate) would indicate that the complex ion was  $[\text{Be}_4\text{BeO}]^{++}$ . The accompanying increase of the anion in the basic solution must, however, somewhat diminish the solubility of the normal salt, although we cannot at such high concentrations calculate the magnitude of this effect. Hence the observed ratio of 4.14 or 4.2 must be greater than the average number of BeO molecules attached to a "beryllated" Be ion.

Now there is good evidence that while the covalency of beryllium cannot exceed 4, it has a strong tendency, particularly in the ionised state, to reach this value. Its soluble salts never have more than 4 molecules of water, but seldom fail to attain this number (the case of the oxalate is discussed below). The same tendency of the atom to pass from the ionised to the covalent state is shown by the low conductivity of the fused chloride and the stability of many of its covalent organic compounds (*e.g.*, the non-ionised basic acetate). Its oxide may thus be expected readily

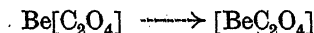
to assume the covalent form  $\text{Be}=\text{O}$ , which could replace the water of crystallisation of the ion :



This replacement will no doubt be incomplete, a series of mixed ions being formed, with the water only partly replaced by  $\text{BeO}$ , so that on the average there will be less than 4  $\text{BeO}$  groups attached to each "beryllated" ion, as we find to be the case.

(2) *Beryllium Oxalate*.—The above hypothesis accounts for the behaviour of basic solutions of the sulphate, selenate, and chloride, and should be applicable to any solution containing beryllium ion : but the behaviour of the oxalate, which increases in solubility by about 3 molecules for every 4 of the oxide added, needs further explanation. This salt is peculiar in many ways. It is unique among the oxalates of bivalent metals in being very soluble in water (nearly 30% at  $25^\circ$ ) : the oxalates of  $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ,  $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Hg}''$ ,  $\text{Sn}''$ ,  $\text{Cr}''$ ,  $\text{Mn}''$ ,  $\text{Fe}''$ ,  $\text{Co}''$ , and  $\text{Ni}$  are all very slightly if at all soluble. It is also almost unique among beryllium salts in not forming a tetrahydrate but only a trihydrate. These facts clearly indicate that it is not a normal oxalate. Further peculiarities which we have found are (1) the conductivity, which even at  $V = 512$  is barely a quarter of that of the sulphate, and at greater concentrations falls to about a sixth, showing that (assuming the ionic mobilities to be about the same) the number of ions formed is only about a quarter of that produced by a normal bi-bivalent salt. (2) The increase of solubility of the salt on addition of oxide is three times as great as with the sulphate or selenate (1 : 1.3 instead of 1 : 4.1). (3) Finally the f. p. experiments show that the number of molecules (including ions) in the solution is not much less than it would be with a normal salt.

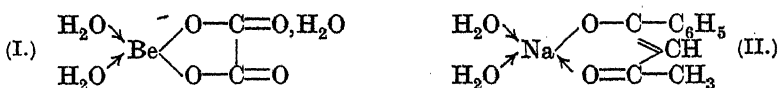
The last fact proves that the compound formed cannot have a high molecular weight, and suggests that the ions have combined to form a non-polar molecule :



which is not improbable in view of the strong tendency (already mentioned) of the beryllium ion to pass into the covalent state, and that of the oxalate ion to form a covalent oxalato-ring, as in Werner's optically active  $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ . On this simple assumption



we should conclude, since the conductivity is reduced to about a quarter, that the solution contains about 3 molecules of oxalato-compound to 1 molecule of salt. The value of  $i$  found by the f. p. method would be  $1 + \frac{1}{4}\alpha$ , if  $\alpha$  is the true degree of dissociation of the salt: the observed values of  $i$  are from 1.2 at 0.05 molar normal to 1.1 at 0.37. This assumption is further supported by the fact that the compound crystallises with 3 molecules of water. The oxalate group is usually monohydrated, both as an ion and in oxalato-compounds: for example, we have  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ;  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ;  $(\text{NH}_4)_2[\text{Hg}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ ;  $\text{K}_3$  and  $(\text{NH}_4)_3[\text{Cr}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ , all salts of kations which are rarely if ever hydrated. Thus one of the  $\text{H}_2\text{O}$  molecules can be attached to the oxalate group. The other two must be joined to the beryllium atom (formula I) if it is to have the stable covalency of 4 which beryllium always attains if possible, and the attainment of which always promotes the formation of covalent links, as in the sodium compound of benzoylacetone (Sidgwick and Brewer, J., 1925, 127, 2383); this when anhydrous is a salt, but it readily takes up two molecules of water and becomes covalent (formula II), as is shown by its then being soluble in hydrocarbons.



A non-polar structure of this kind also makes the formation of solid solutions with oxalic acid less inexplicable.

One peculiarity of the oxalate is unexplained: the large increase (1 : 1.3 instead of 1 : 4.1) of solubility on addition of the oxide. If the latter combines only with the beryllium ion, as it does in the solutions of the strong acid salts, the ratio should be the same in both cases; for on the removal of part of the ions in the "beryllated" form, the equilibrium between the polar and non-polar modifications will be restored. The only explanation would seem to be that the oxide mainly combines with the non-polar form in the ratio 1 : 1 (presumably replacing a molecule of water), but partly also with the ion, as in the sulphate and selenate, thus lowering the ratio of increased solubility to added oxide from 1 : 1 to 1 : 1.3.

The peculiar form of the conductivity curve, which scarcely falls (and if corrected for viscosity, rises) from  $N/5$ - to  $N$ -solution, seems to be without parallel. Since with increasing concentration the molecular conductivity of the true salt must diminish (as it does with all other salts), and likewise presumably the proportion of true salt to non-polar compound, some other reaction must intervene; but it is difficult to see what this is.

Our thanks are due to Messrs. Brunner Mond and Co. for a grant towards the cost of this work, and one of us (N. B. L.) wishes to express his gratitude to the Commissioners of the 1851 Exhibition for a scholarship which made it possible for him to take part in it.

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## CLXVII.— $\omega$ -Mono- and Dibromo-derivatives of Quinaldine and Nitroquinaldines and their Products of Hydrolysis.

By DALZIEL LLEWELLYN HAMMICK.

It has been shown (J., 1923, 123, 2882) that quinaldine can readily be brominated to  $\omega$ -tribromoquinaldine, which can be hydrolysed to quinaldinic acid. A similar route to the corresponding  $\alpha$ -aldehyde and alcohol has now been investigated. Unfortunately, quinaldine cannot be selectively brominated to the  $\omega$ -mono- and dibromo-derivatives;  $\omega$ -tribromo-quinaldine, however, can be reduced to the two other  $\omega$ -bromoquinaldines by the action of the calculated quantities of titanous or stannous chloride in alcoholic or acetone solution.  $\omega$ -Dibromoquinaldine can also be obtained in about 60% yield by the action of excess of sodium arsenite on the tribromo-compound in aqueous-alcoholic solution.

Unlike  $\omega$ -tribromoquinaldine, the mono- and dibromo-derivatives cannot be hydrolysed by the action of acids; even oleum acting at 50° for 12 hours is ineffective. Alkalis yield coloured and resinous products. Silver nitrate, however, in aqueous alcohol converts these derivatives quantitatively into the alcohol and aldehyde respectively.

The mononitro-compounds obtained by the direct nitration of quinaldine have been directly brominated to the  $\omega$ -di- and tri-bromo-derivatives. The latter, on hydrolysis, yield nitrocarboxylic acids which give nitroquinolines on fusion; these have been identified as the 5- and 8-nitro-compounds. The orientation of the products of the direct nitration of quinaldine given by Decker and Remfrey (Ber., 1905, 38, 2773) is thus confirmed.

### EXPERIMENTAL.

$\omega$ -Dibromoquinaldine.—A solution of 23.7 g. (2 mols.) of stannous chloride in 100 c.c. of acetone was slowly added, with constant shaking and cooling, to 20 g. (1 mol.) of  $\omega$ -tribromoquinaldine

(*loc. cit.*) in 250 c.c. of acetone. After 1 hour, the acetone was removed, the solution neutralised with chalk and distilled with steam for about 9 hours. The white, crystalline solid in the distillate crystallised from ligroin in colourless needles, m. p.  $120^{\circ}$  (yield 9.0 g.; 60%) (Found: Br, 52.8.  $C_{10}H_7NBr_2$  requires Br, 53.1%).

*Quinoline-2-aldehyde*.—A mixture of  $\omega$ -dibromoquinaldine (8 g.) in 50 c.c. of boiling alcohol with 8.6 g. (2 mols.) of silver nitrate in 10 c.c. of hot water was boiled for 10 minutes and, after addition of hydrochloric acid and filtration, distilled with steam to remove the alcohol. The solution was now neutralised with chalk and again distilled with steam; the oil that slowly solidified in the distillate separated from ligroin in colourless crystals, m. p.  $71^{\circ}$  (yield 4.6 g.; 100%) (Found: N, 8.9. Calc. for  $C_9H_6N\cdot CHO$ : N, 8.0%). The aldehyde gave an oxime, m. p.  $184^{\circ}$ , and a phenylhydrazone, m. p.  $204^{\circ}$  (compare Kaufmann and Vallette, *Ber.*, 1913, 46, 56).

$\omega$ -*Monobromoquinaldine* was prepared exactly as  $\omega$ -dibromoquinaldine, twice the amount of stannous chloride in acetone solution being used. The *monobromoquinaldine* distilled in steam as a readily solidifying oil and crystallised from ligroin in colourless needles, m. p.  $83^{\circ}$  (Found: Br, 36.1.  $C_{10}H_8NBr$  requires Br, 36.0%). The yield was about 50%.

$\omega$ -*Hydroxyquinaldine* was obtained in quantitative yield from  $\omega$ -monobromoquinaldine by the action of the calculated quantity of silver nitrate in alcoholic solution, exactly as in the preparation of quinoline-2-aldehyde (*vide supra*). The *carbinol* is volatile in steam and crystallises from ligroin or alcohol in fine needles, m. p.  $64^{\circ}$  (Found: N, 8.65.  $C_9H_6N\cdot CH_2\cdot OH$  requires N, 8.8%). It is readily oxidised by chromic acid to quinoline-2-aldehyde.

$\omega$ -*Tribromo-8-nitroquinaldine*.—A solution of quinaldine in excess of cold concentrated sulphuric acid was shaken with the calculated quantity of potassium nitrate crystals until these had dissolved. After heating for 20 minutes on the water-bath, the mixture was poured into water and nearly neutralised with sodium hydroxide, whereupon 8-nitroquinaldine separated (compare Doebner and Miller, *Ber.*, 1884, 17, 1700, who added quinaldine nitrate to concentrated sulphuric acid). A solution of 7 g. of the recrystallised nitroquinaldine (m. p.  $130^{\circ}$ ) in 150 c.c. of glacial acetic acid saturated with sodium acetate was slowly treated with 20 g. (3 mols.) of bromine in 50 c.c. of glacial acetic acid. After 20 minutes' heating on the water-bath, the mixture was poured into water; the  $\omega$ -tribromo-8-nitroquinaldine that separated crystallised from alcohol in faintly yellow needles, m. p.  $132^{\circ}$  (yield 100%) (Found: N, 6.5.  $C_{10}H_5O_2N_2Br_3$  requires N, 6.6%).

8-*Nitroquinaldinic Acid*.— $\omega$ -Tribromo-8-nitroquinaldine (10 g.)

was boiled with 20% sulphuric acid for 10 hours; the 8-nitro-quinaldine acid obtained on pouring the mixture into water and partly neutralising it separated from alcohol in almost colourless crystals, m. p.  $182^{\circ}$  (Besthorn and Ibele, *Ber.*, 1906, 39, 2329, give m. p.  $177^{\circ}$ ). The acid on fusion gave 8-nitroquinoline which, recrystallised from ligroin, melted at  $89^{\circ}$  alone or mixed with a pure specimen.

$\omega$ -Dibromo-8-nitroquinaldine was prepared in the same way as  $\omega$ -tribromo-8-nitroquinaldine, except that two molecular proportions of bromine were used instead of three. The compound crystallises from alcohol in pale yellow needles, m. p.  $183^{\circ}$  (Found: N, 7.9.  $C_{10}H_5O_2N_2Br_2$  requires N, 8.1%).

8-Nitroquinoline-2-aldehyde.—Hydrolysis of  $\omega$ -dibromo-8-nitroquinaldine in the usual way with alcoholic silver nitrate gave about 50% yields of 8-nitroquinoline-2-aldehyde, which crystallises from alcohol in golden needles, m. p.  $152^{\circ}$  (Found: N, 13.7.  $C_9H_5O_2N_2 \cdot CHO$  requires N, 13.9%).

$\omega$ -Tribromo-5-nitroquinaldine.—The second nitroquinaldine, m. p.  $82^{\circ}$ , obtained by the direct nitration of quinaldine is described by Doebner and Miller (*loc. cit.*) as the 7-nitro-compound. The bromination of this substance does not proceed so readily or so smoothly as in the cases already described and the products were obtained in poor yield and mixed with much gummy material. A solution of 11 g. of the above nitroquinaldine in glacial acetic acid saturated with sodium acetate was slowly treated with 28 g. (3 mols.) of bromine in 75 c.c. of acetic acid. After heating for an hour on the water-bath, the mixture was poured into water. The gummy mass that separated was extracted with hot alcohol, from which an oil separated on cooling. The oil solidified on keeping and after recrystallisation from ligroin melted at  $93^{\circ}$  (yield 4 g.; 17%) (Found: N, 6.5.  $C_{10}H_5O_2N_2Br_3$  requires N, 6.6%).

This  $\omega$ -tribromonitroquinaldine was boiled for 10 hours with 20% sulphuric acid. The solution on neutralisation gave an acid which was not purified but, after drying, was decarboxylated by fusion; the product, crystallised from ligroin, melted at  $72^{\circ}$  alone or mixed with pure 5-nitroquinoline. Doebner and Miller's "7-nitroquinaldine" is thus shown to be the 5-nitro-derivative, in accordance with the conclusions of Decker and Remfrey (*loc. cit.*).

Acknowledgment is made of a grant from the Chemical Society which has partly defrayed the cost of this investigation.

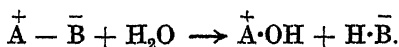
THE DYSON PERRINS LABORATORY,  
OXFORD.

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CLXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part IV. Some Abnormal Reactions as Evidence of the Incipient Ionisation of Certain Hydrogen Atoms in Hydrocarbon Radicals.*

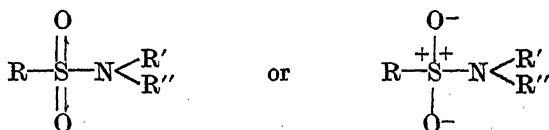
By ERIC LEIGHTON HOLMES and CHRISTOPHER KELK INGOLD.

HYDROLYTIC reactions have often been utilised to diagnose the relative polarities of atoms in combination, the residue which, after fission, appears in association with hydrogen being regarded as negative in comparison with the other :



Observations are recorded in this paper which show that, in certain circumstances, the direction of fission may be changed by altering the experimental conditions even in cases in which the relative polarity of the atoms at the point of fission is fixed by the presence, according to modern theory, of a real electrical charge on one of them.

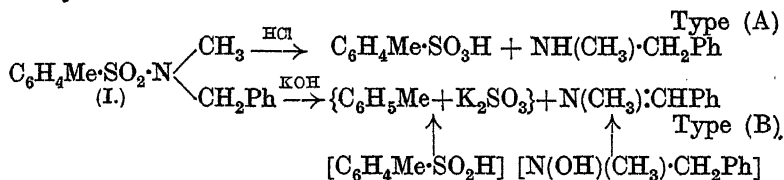
In the following formulæ for the sulphonamide group,



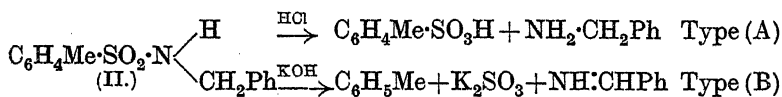
the sulphur atom is represented as carrying a double positive charge, and each of the oxygen atoms a single negative one, whilst the nitrogen atom remains neutral. That is to say, the sulphur atom is necessarily positive with respect to the nitrogen atom, and, accordingly, a sulphonamic acid and an amine,  $\text{R} \cdot \text{SO}_2 \cdot \text{OH} + \text{H} \cdot \text{NR}'\text{R}''$ , are the expected products of fission.

*p*-Toluenesulphonbenzylmethylamide (I) behaves in this way on treatment with mineral acids, but with concentrated alkalis it gives products equivalent, as regards state of oxidation, to a sulphinic acid and a hydroxylamine,  $\text{RSO}_2 \cdot \text{H} + \text{HO} \cdot \text{NR}'\text{R}''$ . Two of the products obtained, toluene and sulphurous acid, must almost certainly have been formed from *p*-toluenesulphinic acid, which is known to undergo decomposition into these substances in the presence of strong alkalis; whilst the third, benzyldidenemethylamine, is the expected dehydration product of benzylmethylhydroxylamine. The possibility of its formation from the hydroxylamine under the conditions used was controlled by subjecting the

dibenzylhydroxylamine to the same conditions, when benzylidenebenzylamine was obtained.

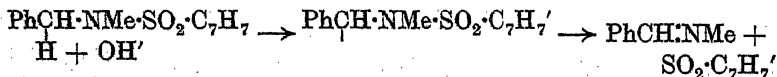


Precisely analogous decompositions were observed in the case of *p*-toluenesulphonbenzylamide (II), only in this instance the benzylideneimine was largely hydrolysed to ammonia and benzaldehyde, which underwent further change into benzoic acid (and, probably, benzyl alcohol) under the action of the alkali.



In attempting to account for these remarkable reactions (Type B), we have formed the view that the decomposition with alkali, essentially an attack by negative hydroxyl ions, commences not at the sulphur atom (in spite of its positive polarity), but at a carbon-hydrogen linking in an alkyl group attached to the nitrogen atom.

Owing to the diminished additive power of the ionised double linkings in the sulphonic acid group (they are single linkings from the standpoint of co-valency), we regard the sulphur atom as largely protected from the direct attack of hydroxyl ions by the additive mechanism discussed by Gane and Ingold (this vol., p. 10) in connexion with the alkaline hydrolysis of carboxylic esters. The attack therefore commences, in the above instances, at the  $\text{CH}_2$  group in which, we believe, the hydrogen atoms are in a condition of incipient ionisation, ready to give up their nuclei (but not their electrons) to a hydroxyl ion to form undissociated water (compare Goss and Ingold, J., 1925, 127, 2777). As the extraction of a hydrogen ion from the benzyl group proceeds, a charged unsaturated residue is left, which in rearrangement necessarily gives a Schiff's base and splits off the ion of a sulphinic acid :



The changes here represented as taking place in steps are regarded as being actually continuous and simultaneous. According to this view, the hydroxylamine does not intervene in the formation of the Schiff's base, but the ready dehydration of hydroxylamines to

Schiff's bases under the action of alkali can be explained by a somewhat similar mechanism.

In order to test the view that the attack by hydroxyl ions commences at the benzyl group, the sulphonamides  $C_6H_4Me \cdot SO_2 \cdot NMePh$  (III) and  $C_6H_4Me \cdot SO_2 \cdot NHPh$  (IV) were treated with potash under the same conditions.

In case (III), an opportunity still remains for the suggested mechanism to function if the attack could begin at one of the hydrogen atoms of the methyl group: the initial products would be toluenesulphinic acid and methyleneaniline, and the formation of these would be shown by the identification of toluene, sulphite, formaldehyde, and aniline. However, for reasons indicated below, the extraction of a hydrogen nucleus (ion) from the methyl group would be expected to offer much greater difficulty than its extraction from the benzyl group in examples (I) and (II). Consequently fission of Type (B) should occur only to a small extent or not at all. Actually a reaction of Type (B) can be detected, but the principal change is that which corresponds with Type (A).\*

In case (IV), the mechanism by which reaction (B) has been explained cannot operate at all, and actually there is no evidence of fission to form a sulphinic acid, the observed decomposition being wholly of type (A). The occurrence of reaction (A) in the last two cases and, under the influence of acids (hydrogen ions), in all four cases, we attribute to the direct ionic fission of the sulphur-nitrogen bond, a process which occurs only when more facile modes of decomposition are impossible.

In our opinion, then, the remarkable action of alkalis on the sulphonamides (I) and (II) provides clear evidence of the occurrence of the benzyl hydrogen atoms in a state of incipient ionisation. The cause of this condition we attribute to general polarity (Lewis), the inherent tendency of hydrogen to function as a positive ion (separate as a proton) being augmented by the presence of a group such as phenyl, which is assumed to be capable of drawing electrons towards itself, thus leaving the hydrogen nuclei in a loosely-combined, active state. This condition obtains in all  $\psi$ -acids, and bears on the questions of hydrogen-tautomerism and meta-substitution (next paper). The opposite condition, in which a group, by allowing electrons to be withdrawn from it, increases a pre-existing, inherent tendency for an atom or group (e.g., hydroxyl) to separate as a negative ion, is similarly illustrated in  $\psi$ -bases, mobile hydroxyl tautomerism, and ortho-para-substitution (see next paper). In the first case, the activating group may be said to act as an "electron-

\* Excepting that, of course, *p*-cresol and potassium sulphite are obtained in place of *p*-toluenesulphonic acid.

sink," and in the second as an "electron-source," towards the rest of the molecule :



### EXPERIMENTAL.

(I) *Hydrolysis of p-Toluenesulphonbenzylmethylamide* (I).—The amide (8 g.) was cautiously warmed with moist fused potassium hydroxide (20 g.) during about 0.5 hour, the volatile decomposition products being distilled towards the end of that period. The distillate, on being dried and redistilled, gave two fractions, b. p. 110—120° (a) and b. p. 180—190° (b). Fraction (a) (2.5 g.) had the odour of toluene, on redistillation boiled close to 110° and on nitration yielded 2 : 4-dinitrotoluene (m. p. 71°), which was identified by comparison with an authentic specimen. Fraction (b) (3.75 g.) consisted essentially of benzylidenemethylamine (Found : C, 80.4; H, 7.6. Calc. : C, 80.7; H, 7.0%). On treatment with dilute hydrochloric or nitric acid, an oil separated, which was identified as benzaldehyde by its odour, and semicarbazone (m. p. 224°, which is the correct m. p., not 214° as stated in the literature). The hydrochloric acid solution on evaporation gave methylamine hydrochloride (m. p. 226°; mixed m. p. with genuine specimen 226°. Found : Cl, 52.0. Calc. : Cl, 52.6%), and similarly, the nitric acid solution yielded methylamine nitrate (m. p. 99—101°; mixed m. p. with genuine specimen 99—101°. Found : C, 13.0; H, 7.0. Calc. : C, 12.8; H, 6.7%). An authentic specimen of benzylidenemethylamine prepared as described by Zaunschirm (*Annalen*, 1888, **245**, 281) behaved in the same way. The residual alkali on dilution and acidification evolved sulphur dioxide.

(II) *Hydrolysis of p-Toluenesulphonbenzylamide* (II).—The hydrolysis of 8 g. of this amide was carried out as in the previous case, but a considerable amount of ammonia was evolved. The volatile liquid products were shaken with dilute acid, and the undissolved portion was distilled; 0.9 g. of pure toluene was then obtained. The acid extract deposited benzaldehyde and gave ammonia on being made alkaline, so that the presence of benzalimine in the original distillate may be inferred. The residual alkali was extracted with ether to remove any neutral or basic products (which, however, were absent) and then acidified. The solution was boiled to expel most of the sulphur dioxide and then extracted with ether. The solid residue (1.5 g.) from the ether consisted largely of benzoic acid contaminated by some substance or substances



which instantaneously decolorised permanganate and could only be removed by distillation (b. p. 240—245°/750 mm.) followed by several crystallisations from carbon disulphide and ligroin. (Found: C, 68·6; H, 5·0; *M*, 120. Calc.: C, 68·9; H, 4·9%; *M*, 122). *p*-Cresol was searched for, but could not be detected.

(III) *Hydrolysis of p-Toluenesulphonphenylmethylamide* (III).—This *amide*, m. p. 93°, was prepared by the action of *p*-toluenesulphonyl chloride on a sample of Kahlbaum's methylaniline which qualitative tests showed to contain no trace of a primary base. The hydrolysis of 8 g. was carried out as before, the gas evolved being passed through Schiff's reagent acidified with dilute sulphuric acid, when a permanent red colour was produced. The volatile liquid products were separated into neutral and basic portions. The former was small in amount, had the odour of toluene, and yielded a solid which was identified as unchanged *amide*. The basic portion (2·9 g.) had b. p. 185—190°, and gave the qualitative reactions both of a primary and of a secondary base, and both aniline and methylaniline were identified as their *p*-toluenesulphonyl derivatives (Hinsberg's method of separation). The alkaline residue on acidification evolved sulphur dioxide, and extraction with ether yielded a dark oil which slowly deposited a small quantity of crystals, m. p. 190—200° (0·1 g.). After crystallising twice from water, these yielded prisms, m. p. 210°, which were identified as *p*-hydroxybenzoic acid by analysis (Found: C, 60·5; H, 5·0. Calc.: C, 60·8; H, 4·4%) and comparison with a genuine specimen. The oil from which the crystals separated was distilled (b. p. 190—195°) and was identified as *p*-cresol by conversion into its benzoyl derivative. *p*-Hydroxybenzoic acid is known (Barth, *Annalen*, 1870, 154, 359) to be formed by the action of potassium hydroxide on *p*-cresol.

(IV) *Hydrolysis of p-Toluenesulphonanilide* (IV).—This *amide* (8 g., m. p. 99°) was treated as in the previous cases and the products were separated similarly. The volatile portion of the hydrolysis products (3·7 g.) consisted of aniline, whilst the alkaline residue yielded *p*-cresol (3·0 g.) and *p*-hydroxybenzoic acid (0·1 g.).

(V) *Action of Potassium Hydroxide on Dibenzylhydroxylamine*.—Dibenzylhydroxylamine (5 g.), prepared as described by Schramm (*Ber.*, 1883, 16, 2104), was treated in the usual way, and the volatile products were isolated by distillation at 5 mm. Redistilled at 2 mm., these gave a small fraction (*a*) boiling up to 160°, and a main fraction (*b*), b. p. 160°. Fraction (*b*) consisted of benzylidenebenzylamine (Found: C, 85·8; H, 7·2. Calc.: C, 86·1; H, 6·7%), since on treatment with dilute hydrochloric acid it gave benzaldehyde (identified as its semicarbazone) and benzylamine (identified as hydrochloride). Fraction (*a*), although too small to purify, must

have contained much of the same azomethine, since the same amine and aldehyde were obtained from it.

We wish to thank the Chemical Society for a grant, with the aid of which part of the cost of this research has been met.

THE UNIVERSITY, LEEDS.

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CLXIX.—*The Nature of the Alternating Effect in Carbon Chains. Part V. A Discussion of Aromatic Substitution with Special Reference to the Respective Rôles of Polar and Non-polar Dissociation ; and a further Study of the Relative Directive Efficiencies of Oxygen and Nitrogen.*

By CHRISTOPHER KELK INGOLD and EDITH HILDA INGOLD.

THE preceding parts of this series describe a partial examination of the theories of the alternating polarisation of atoms (A), and of the alternating affinity content of valencies (B), as applied to aromatic substitution :



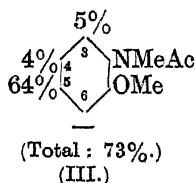
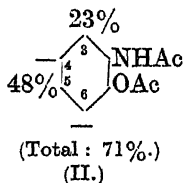
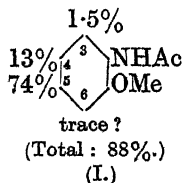
The criterion adopted was that, according to the first view, the more electronegative atoms of the series N, O, F, should produce the larger effects ( $F > O > N$ ), whilst, according to the second, the reverse should hold, the most "unsaturated" atom being the most potent ( $N > O > F$ ).

In Part III, a comparison of benzylamines and benzyl ethers was recorded, from which it was concluded that nitrogen is more effective than oxygen, which appeared to agree with theory (B). Observations have since been made, however, which show that even this theory is not adequate without extension, and that special factors must enter into the problem of the orientation of substances in which the "key-atom" is separated from the nucleus by a chain of one or more carbon atoms. It is therefore necessary to examine the application of other considerations. Nevertheless, the general conclusion previously reached with regard to the directive efficiencies of oxygen and nitrogen accords with that to which the present experiments on the nitration of derivatives of *o*-aminophenol have led.\*

The results of these experiments are represented in the following

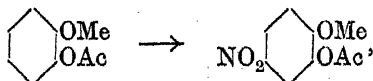
\* The case of O versus F is dealt with in the following paper.

formulae, in which the figures connote material accounted for in units per cent. of the theoretical :



It will be clear from these data that whether we disregard *o*-substitution as possibly subject to special influences and consider only substitution in positions 4 and 5, or whether we accept the total *op*-direction by each group as the best measure of its efficiency, the group containing nitrogen is the more effective, for (except in case II, in which the total recovery is not very satisfactory) more than 50% of the material was accounted for as the 5-nitro-derivative. Strictly speaking, these conclusions apply only to the cases dealt with, but it seems likely that they will hold fairly generally in the simpler analogous cases. Possible abnormality arising from indirect substitution *via* the amino-hydrogen atom is controlled by case (III), the results of which differ little from those of (I), and the differing effects of alkyl and acyl groups in modifying the directive efficiency of an oxygen or nitrogen atom are partly controlled by example (II). In any case, other data show that the distribution of alkyl and acyl groups in examples (I) and (III) is such as would handicap the nitrogen atom.

The depressing effect of acyl as compared with alkyl groups on *op*-directive power may be illustrated by the 4-nitration of acetyl-guaiacol,



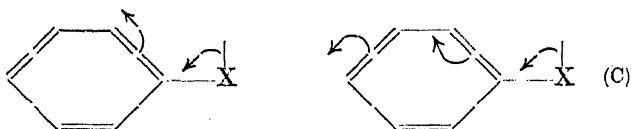
and is of importance in connexion with Smedley's formula for the carboxyl group (J., 1909, 95, 231), a modernised interpretation of which would involve the recognition of a betaine-like phase,\* the bond joining the oxygen atoms being an electrovalency. In the carboxylamide group, the nitrogen atom will necessarily constitute the positive end of the betaine linking, and thus forms arise which (on any theory, and by analogy also) would be expected to diminish the tendency towards *op*-substitution :



\* Or a condition corresponding with partial conversion into such a phase.

The low value found by Sugden (J., 1924, **125**, 1185) for the parachor of the group  $\text{CO}_2$  in carboxylic esters would then be attributed to shrinkage arising from electrostatic attraction.

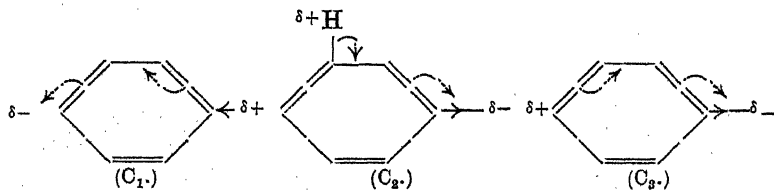
The above results, whilst they appear inconsistent with the idea of alternating polar charges (A), agree either with Flürscheim's theory of alternating affinity content (B), or with Robinson's theory (*Chem. and Ind.*, 1925, **44**, 456) of *op*-substitution by electronic displacement in conjugated systems (C).<sup>\*</sup> This theory leads to much the same key-efficiency series as Flürscheim's, if residual affinity be interpreted as an indication of the presence of loosely held, active electrons. The arrows represent the assumed electron displacements originating in a latent valency:



It will be obvious that the distribution of forces here involved is qualitatively the same as that in Flürscheim's theory, the completed change (C) corresponding with his figure for *op*-substitution:



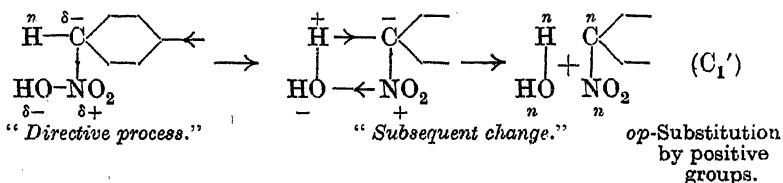
In applying these suggestive ideas to the cases of substitution previously described, we would regard the above formulæ as expressing only the direction of imaginary gross changes which actually do not at any time proceed to more than a limited (in some cases an exceedingly small) extent. This interpretation is placed upon the formulæ partly to cover the case of direction by methyl, which, we assume, has not electrons available for a complete co-valency change (even a momentary one), and is expressed by a slight change of symbolism ( $C_1$ ),<sup>†</sup> the dotted arrows representing electronic strain:



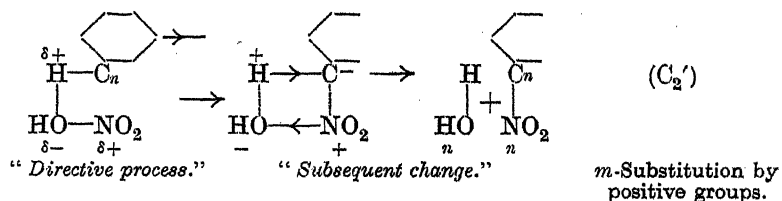
<sup>\*</sup> Since the above was written, a fuller statement has become available (this vol., p. 401).

<sup>†</sup> In this formula, and those which follow,  $\delta+$  and  $\delta-$  are used to signify small fractions of a unit charge;  $n$  represents neutrality, and the signs  $+$  and  $-$  connote unit charges.

It may then be supposed that the *incipient* negative polarisation of the *o*- and *p*-carbon atoms (in different electromeric phases) would be sufficient to attract the positive end of an *incipiently* ionised molecule (*e.g.*, nitric acid or chlorine).<sup>\*</sup> This corresponds with Flürscheim's theory of molecular addition at a point by *residual* (not real) valencies, and may be termed the "directive process." This having occurred, the tendency for hydrogen to unite as a *positive ion* (compare Part IV) with, for instance, hydroxyl or chlorine acting as a negative one, would lead to reaction in a four-cycle † (the "subsequent change") with the unit electron displacements shown, and without the necessity for any further electronic displacement in the benzene system itself :



The case of *m*-substitution is regarded as an effect produced by groups which tend to withdraw electrons from the nucleus (*loc. cit.*). Combining this suggestion with the evidence, discussed in Part IV, of incipiently ionised hydrogen in combination with carbon, and of its extraction in the form of a true ion by the hydroxyl ion, the view may be expressed (formula C<sub>2</sub>) that the meta-hydrogen atom in these cases reaches a state of incipient ionisation, owing to a pull on the electrons involved in its linking with the nucleus. The meta-carbon remains approximately neutral, and the attack of an incipiently ionised reagent therefore begins at the positively polarised hydrogen atom : ‡



<sup>\*</sup> Since ortho- versus para-substitution is not now under consideration, the operation of direct exchange with the *p*-position is disregarded to abbreviate description.

† Or, a third molecule might enter into the reaction, giving a six-cycle.

‡ The assumption of a less direct type of activation preceding *m*-substitution is consistent with the generally smaller velocities of these reactions as compared with *op*-substitutions.

Formula  $C_3$  corresponds with the direction of negative ions to the *op*-positions (Robinson, *loc. cit.*) and need not be expanded, since the "subsequent change" may pursue different paths (leading to the same goal) according as the ionisation of the reagent is incipient, or actual \* (hydrolysis of *p*-chloronitrobenzene).†

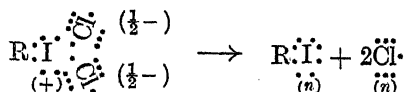
In applying these three principal directive effects, we bear in mind that they can determine only the (reversible) *initial attraction* of the reagent, and that the substitution cannot ensue unless the conditions necessary for the "subsequent change" are present. An essential condition in cases  $C_1$  and  $C_2$  is that the displaced atom should be one (*e.g.*, hydrogen) which tends to function as a *positive* ion, and can be extracted from the molecule as a positive ion under the conditions employed. Similarly, in  $C_3$  the "subsequent change" can occur only if the expelled atom is one (*e.g.*, chlorine) which tends to function as a *negative* ion and is capable of being removed in this form by the reagent used. The importance of these auxiliary conditions may be illustrated by the fact that, neglecting them,  $C_3$  necessitates that nitrobenzene and nitric acid should yield *p*-nitrophenol and nitrous acid, and many similar absurdities.

Taking count of "general" electronic restraint, subsidiary directive effects may be perceived which need not be stated. It has also to be remembered that the dissociation of a reagent into *neutral* atoms, or radicals, may lead to substitution in positions determined by the consideration that those neutral atoms (*e.g.*, Cl) which have to *gain* electrons to form their stable ions will seek out negative centres, and in this respect simulate a *positive* group, and *vice versa*. This may well be the mechanism of chlorination by phosphorus pentachloride, iodine trichloride and aryl iodide di-

\* In this case there can be no reaction in a cycle, and the "subsequent change" may involve a complete reversible conversion into the quinonoid condition.

† Whether a particular group will act as an "electron-source" or "electron sink" (this vol., p. 1307) towards the benzene ring is, in general, determined by the fact that electronic strain can in each case operate only in one way if all octets are to be preserved. Thus -OMe is necessarily a source, and -CH<sub>2</sub>O necessarily a sink so far as principal directive effects are concerned. Also, a fluorine atom directly attached to the ring can only act as a source by the mechanism considered, although in saturated chains it should act as a sink, tending towards separation as a negative ion (general polarity). For this reason, when directly joined to the nucleus, it acts as a source only with reluctance, *i.e.*, is only feebly *op*-directing (compare following paper). Direction by methyl and vinyl are special cases which do not appear to be capable of determination *a priori* by generally recognised electronic principles, although *experiment* indicates that each functions as a source in aromatic substitution.

chlorides, each of the two loosely-held chlorine atoms in these compounds being regarded as bound by a single electron (compare Prideaux, *Chem. and Ind.*, 1923, 42, 672) and as in a state of incipient *atomic* dissociation of the following kind : \*



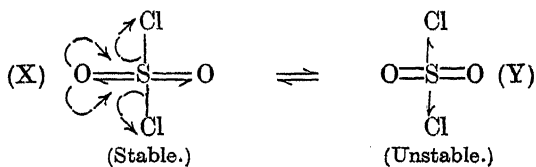
Again, the equation indicates only the direction, and not the extent, of the change (*i.e.*, dissociation) necessary to initiate reaction. Thus it happens that chlorine, although *negative* (0.5 unit charge) in the original group, tends to separate as a *neutral* atom which so desires an electron that it simulates a *positive* group. Thus the apparent anomaly of negative chlorine leaving positive iodine or phosphorus to become attached to negative carbon is explained. On this view, chlorination through the neutral atom can take place in system C<sub>1</sub>, but not in C<sub>2</sub> or C<sub>3</sub>, since only the first contains a negative centre; accordingly, phosphorus pentachloride readily chlorinates anisole in the *p*-position, but has no action on nitrobenzene.

The apparently anomalous introduction of the "negative" hydroxyl group into the *op*-positions of phenols, etc., in electrolytic oxidation is evidently an analogous phenomenon. If the substance oxidised is stable to alkalis (as is usually the case), the hydroxyl *ion* has, of course, no action; but when the anode strips an electron from it, it becomes a neutral free radical with a septet, and hence attacks the incipiently negative carbon atoms of the aromatic compound. Again, mechanism C<sub>1</sub> can function (*op*-substitution) but not C<sub>2</sub> (*m*-substitution), which corresponds precisely with ascertained fact: many electrolytic *op*-oxidations are on record, but, so far as we are aware, no *m*-oxidations.

Sulphuryl chloride may be regarded as having two electromeric forms, the stable one containing two semipolar double bonds (X), and the other only one semipolar double bond and two semipolar single bonds (Y). It is the latter which contains the labile chlorine, and it would be this form rather than the first which is concerned in chlorination by sulphuryl chloride. The action of this reagent is therefore not anomalous (compare Flürscheim, *Chem. and Ind.*,

\* The small electrical conductivity of phosphorus pentachloride in nitrobenzene (Holroyd, Chadwick, and Mitchell, J., 1925, 127, 2492) appears to favour this view, as against the ionic structure  $(\text{PCl}_4)^+\text{Cl}^-$ . The bonds by which the labile chlorine atoms are held might be termed "semi-polar single bonds" and written  $\rightarrow$  to avoid the use of signs such as  $\frac{1}{2}+$  and  $\frac{1}{2}-$ .

1925, 44, 172, 427; Robinson, *ibid.*, p. 259); it is another instance of attack by a neutral radical:



Thus, in conformity with the two known kinds of dissociation of co-valency compounds, it is suggested that both polar and non-polar dissociation may be concerned in aromatic substitution, the main determining condition being the electronic constitution of the reagent. This view, we think, interprets the data more consistently than is possible by means either of a purely ionic or of a purely non-ionic conception; it is advanced, however, mainly to facilitate discussion, for it is clear that the main principles, even if true, must be held as subject to possible modifications arising from other influences.

#### EXPERIMENTAL.

##### (I) Nitration of Aceto-*o*-anisidide.

Mulhauser (*Annalen*, 1899, 207, 242) nitrated aceto-*o*-anisidide and obtained a mononitro-derivative, m. p. 143°. Meldola, Woolcott, and Wray (*J.*, 1896, 69, 1330) found m. p. 145–146°, and suggested that it was the 5-nitro-derivative (for numbering, see Formula I, p. 1311) but did not prove this orientation. The Fabrik de Produits Chimique de Thann et de Mulhause (D.R.-P. 98637) stated that the substance was in reality a mixture of two isomerides, m. p. 153° and 131–132° respectively. We find that, whilst the first of these is a pure compound, identical with 5-nitroaceto-*o*-anisidide synthesised by Vermeulen (*Rec. trav. chim.*, 1905, 25, 12), the second is a mixture containing, besides the 5-nitro-compound, its 4-nitro-isomeride, m. p. 174–175°. Small quantities of the 3-nitro-compound, m. p. 158–159°, and, probably, of the 6-nitro-compound, m. p. 103–104°, are also produced in the nitration. The 4-nitro-compound was synthesised by Meldola, Woolcott, and Wray (*loc. cit.*) and by Vermeulen (*loc. cit.*). The properties of the 3- and 6-nitro-derivatives and their orientation are described below.

*Qualitative Separations.*—(I) A well-cooled solution of 1.5 c.c. of nitric acid (*d* 1.5) in 5 c.c. of acetic anhydride was added to the paste obtained by cooling a solution of 5 g. of acetanisidide in 10 c.c. of acetic anhydride to 0°. Heat was generated, but the temperature was not allowed to rise above 45°. The mixture was kept at the ordinary temperature for 24 hours and, after addition of water,



shaken to destroy acetic anhydride. The solid product (6.0 g.) was subjected to about 20 fractional crystallisations from absolute alcohol, which yielded the following apparently pure substances, here named in the order of their appearance: (a) large, stout, prisms, m. p. 153—154° (2.0 g.); (b) long, silky needles, m. p. 173.5—175° (0.1 g.); (c) rosettes of small needles, m. p. 129—131° (0.5 g.). By direct comparison (a) was shown to be 5-nitroaceto-*o*-anisidide, and (b) 4-nitroaceto-*o*-anisidide. The crystals (c) we assume to be identical with the product, m. p. 131—132°, described in D.R.-P. 98637, but direct comparison showed that it was neither 3-, 4-, 5-, nor 6-nitroaceto-*o*-anisidide. It had the correct composition (Found: C, 51.7; H, 4.9.  $C_9H_{10}O_4N_2$  requires C, 51.4; H, 4.8%), and, since its m. p. was depressed by the addition of the 3- and 6-nitro-compounds and raised by the addition of either the 4- or the 5-derivative, we regard it as a difficultly separable mixture of the last two isomerides. After hydrolysis of the acetyl group, the corresponding free bases can be separated in the pure condition, the 5-derivative being isolated in larger quantity than the 4-isomeride.

(II) Another experiment using 40 g. of aceto-*o*-anisidide was carried out in the same way, excepting that the most soluble fractions obtained after a rough separation were combined with the product isolated by neutralising the dilute acetic acid solution and extraction with ether, and fractionally crystallised as completely as possible. Fractions identical with (a) and (c) were obtained, and also a very small amount of a substance, m. p. 99—103°, which did not depress the m. p. (103—104°) of synthetic 6-nitroaceto-*o*-anisidide, but was insufficient for analysis.

Further experiments did not lead to the isolation of the 3-isomeride, although the presence of this was proved indirectly.

*3-Nitroaceto-o-anisidide*.—3-Nitro-*ON*-diacetyl-*o*-aminophenol (see below) (0.5 g.) was treated at 30—40° with 2 c.c. of cold 2*N*-sodium hydroxide and the deep red solution was shaken with successive small quantities of methyl sulphate, additional alkali being added as it became necessary. When the red colour had given place to lemon-yellow, the precipitate was collected and crystallised from alcohol; pale yellow needles, m. p. 158—159°, were then obtained (Found: C, 51.7; H, 4.8.  $C_9H_{10}O_4N_2$  requires C, 51.4; H, 4.8%). The m. p. of this substance was depressed 20° to 60° by the addition of its isomerides, 4-, 5-, and 6-nitroaceto-*o*-anisidide. Since the 4-, 5-, and 6-compounds were all synthesised by methods which showed their constitutions, the orientation of the 3-derivative follows. It was confirmed by conversion of the substance into 3-nitroguaiacol by boiling for 36 hours with 2*N*-sodium hydroxide

and acidifying the resulting solution. This guaiacol was not synthesised for comparison, but the specimen obtained had the m. p. (60—61°) and properties recorded in the literature, and had the large volatility with steam characteristic of *o*-nitrophenols (see below). The base, 3-nitro-*o*-anisidine, was obtained by heating the acetyl derivative for 30 minutes with 20% hydrochloric acid on the steam-bath and extracting the product with ether from the solution basified with ammonia. The same base was obtained along with 3-nitroguaiacol when the acetyl compound was boiled for 6 hours with 2*N*-aqueous sodium hydroxide. It separated from alcohol in bright scarlet needles, m. p. 75—76° (Found: C, 50.0; H, 4.8.  $C_7H_8O_3N_2$  requires C, 50.0; H, 4.8%).

4-Nitroaceto-*o*-anisidide.—This was prepared by Meldola, Woolcott, and Wray's method (*loc. cit.*). It had m. p. 174—175°, and the corresponding free base, m. p. 117—118°. On boiling either the base or its acetyl derivative for 30 hours with 2*N*-aqueous sodium hydroxide under the conditions in which the 3- and 5-isomerides yield nitroguaiacols, deep-seated decomposition took place, although some unchanged base was recovered. A specimen of 4-nitroguaiacol, m. p. 103—104°, was prepared by the direct nitration of acetylguaiacol (Reverdin and Crepieux, *Ber.*, 1903, 36, 2258; 1906, 39, 4232; Paul, *Ber.*, 1906, 39, 2779) but, even on seeding with a crystal of this, the same compound could not be obtained from the small quantity of acidic tar isolated from the product of hydrolysis. A few crystals, m. p. 80—90°, were obtained, but the amount was insufficient for purification.

5-Nitroaceto-*o*-anisidide.—Vermeulen's method (*loc. cit.*) was used for the preparation of this substance, which was obtained in large, pale yellow, nearly cubical prisms, m. p. 153—154°. On cooling a solution of it in warm concentrated hydrochloric acid, a sandy precipitate was obtained, which on treatment with water turned yellow. Its solution in much boiling water was rendered alkaline with sodium carbonate and cooled; the free base then separated as golden-yellow, flattened needles, m. p. 139—140°. On boiling for 36 hours with 2*N*-aqueous sodium hydroxide, either the acetyl derivative or the base is converted fairly smoothly into 5-nitroguaiacol, which is precipitated on acidification, the filtrate containing a further quantity isolable by extraction with ether. This nitroguaiacol had m. p. 99—100° and depressed the m. p. of 4-nitroguaiacol.

6-Nitroaceto-*o*-anisidide was synthesised from 2 : 6-dinitroanisole by partial reduction and acetylation of the nitro-base. An alcoholic solution of 2 : 6-dinitroanisole was treated for 30 minutes with a rapid stream of hydrogen sulphide. During the first 10 minutes

much heat was developed. Water was added, and the base extracted from the precipitate by digestion with 20% hydrochloric acid, from which it was reprecipitated on addition of ammonia. Having been dried as rapidly as possible, the crude base was repeatedly extracted with boiling ligroin until the extracts failed to crystallise on cooling. 6-Nitro-*o*-anisidine was thus obtained as bright yellow, flattened needles, m. p. 65–66°, a further quantity being recoverable from the ligroin solution. An additional crystallisation from ligroin raised the m. p. to 67° (Found: C, 50.0; H, 4.7.  $C_7H_8O_2N_2$  requires C, 50.0; H, 4.8%). The *acetyl* derivative was obtained by boiling the base for 2 hours with acetic anhydride, and crystallised from methyl alcohol or dilute acetic acid in pale yellow prisms, m. p. 103–104° (Found: C, 51.5; H, 4.8.  $C_9H_{10}O_4N_2$  requires C, 51.4; H, 4.8%). Attempts to convert either of these substances into 6-nitroguaiacol by the method used for the corresponding reaction in the 5-series led to deep-seated decomposition and products from which no crystalline substance could be isolated.

*Attempted Estimation of the Proportions of the Isomerides.*—(i) The nitration of 40 g. of aceto-*o*-anisidide was carried out in acetic anhydride as described above and the product allowed to crystallise over-night, when 9.1 g. of the 5-nitro-compound separated. The acetic anhydride was then removed by desiccation at a low pressure over potassium hydroxide. The residue was fractionally crystallised from alcohol, and a further quantity of 5-nitro-compound (1.5 g.) and some 4-nitro-compound (1.0 g.) were obtained. The weights are those of the fully purified isomerides. The unseparated residue was hydrolysed with hydrochloric acid and the bases were fractionated from alcohol, the 5-nitro-base (3.7 g.) and the 4-nitro-base (0.65 g.) being isolated. The unseparated portions were reacylated and by further crystallisation the 5-nitro-*acetyl* derivative (2.1 g.) and its 4-isomeride (1.4 g.) were obtained. About 1 g. of a mixture remained which was not resolved. The total pure substances isolated corresponded with 68% of 5-nitro-compound and 13% of 4-nitro-compound.

(ii) In a similar experiment to the above, 37% of 5-nitroaceto-*o*-anisidide separated from the acetic anhydride. The residue obtained on complete evaporation was boiled for 36 hours with 10 times its weight of 2*N*-sodium hydroxide, and the resulting solution diluted to dissolve the red, rather sparingly soluble sodium salt of 5-nitroguaiacol, and extracted with ether. The bases thus recovered (2.8 g., and in another similar experiment 3.5 g.) were contaminated with products of deep-seated decomposition, but yielded some crystalline 4-nitroanisidine. On acidification of the alkaline solution 5-nitroguaiacol (11.2 g.), m. p. 96–99°, was obtained, and the

mother-liquors yielded a mixture of guaiacols, which were recovered by extraction with ether and purified and partly separated by distillation in steam. Experiments with artificial mixtures of 3-nitroguaiacol and 5-nitroguaiacol showed that the former passed over completely in the early stages of distillation, but that a small quantity of the latter was present in all fractions. Further experiments to determine the volatility of 5-nitroguaiacol in steam indicated that, under the usual conditions of distillation, the steam reaching the condenser is not quite saturated; but by working under uniform conditions as regards apparatus and rate of distillation a fairly consistent figure of 1.20 g. per litre was obtained and this was regarded as sufficiently accurate in experiments carried out under like conditions. In the distillation of the mixed guaiacols described above, the first 500 c.c. of distillate yielded 1.26 g., m. p. 60–80°, whilst the succeeding 500 c.c. fractions each gave 0.6 g., m. p. 97–100°, so that 0.66 g. of the more volatile 3-nitroguaiacol was assumed to be present in the original mixture. This corresponded with a yield of 1.5%, whilst the total quantity of 5-nitroguaiacol was equivalent to 37% of the theoretical, a further 37% of 5-nitroaceto-*o*-anisidine having been also obtained as described above.

Combining these results, it follows that in the original nitrations the 5-nitro-derivative was formed to the extent of at least 74%, the 4-nitro-compound to the extent of at least 13% and the 3-isomeride to the extent of about 1.5%, a small quantity of the 6-compound probably also being produced. The total yield was 88.5%.

## (II) Nitration of *ON*-Diacetyl-*o*-aminophenol.

The nitration of *ON*-diacetyl-*o*-aminophenol was carried out by Meldola, Woolcott, and Wray (*loc. cit.*), who isolated the 5-nitro-derivative, m. p. 189°, which they definitely oriented. They did not notice the formation of a second isomeride. Our attempts to follow their method yielded either dinitro-compound, or mixtures of unchanged material with mono- and di-nitro-derivatives. On the other hand, treatment with the theoretical quantity of nitric acid in warm acetic anhydride led to smooth mononitration.

**Dinitration.**—A solution of the diacetyl compound (10 g.) in a mixture of 40 c.c. of ordinary concentrated nitric acid and 20 c.c. of fuming acid at –5° was kept for 2 hours at 2–4°, and ice then added. The precipitate, which was collected on the next day, crystallised from boiling water in long, yellow needles, m. p. 202°. Since analysis (Found: C, 40.2; H, 3.2; N, 17.8.  $C_8H_7O_6N_3$  requires C, 39.8; H, 2.9; N, 17.5%) indicated that one acetyl group had been eliminated, and the substance gave an immediate

precipitate of the red potassium salt when treated in alcoholic suspension with cold dilute potassium hydroxide solution, we regard it as 3:5-dinitro-*N*-acetyl-*o*-aminophenol. The compound was not definitely oriented, but the positions of the nitro-groups are inferred from the study of the mononitration of diacetylaminophenol described below.

*Mononitration. Qualitative Separation of Isomerides.*—The paste obtained by cooling a solution of diacetyl-*o*-aminophenol (20 g.) in acetic anhydride (40 g.) to 15° was treated gradually with an ice-cold mixture of 5 c.c. of nitric acid (*d* 1.5) and 20 c.c. of acetic anhydride. The crystals dissolved and the temperature rose rapidly, but was kept from exceeding 35° by external cooling. When self-heating had ceased, the mixture was allowed to cool to the ordinary temperature; a stiff paste of yellow crystals then formed. Several hours later, the acetic anhydride was destroyed by shaking with water, and the solid product, m. p. 140–160°, collected. This was fractionally extracted with boiling alcohol; the less soluble product, m. p. 165–180°, thus obtained, after four crystallisations from alcohol, yielded very characteristic, long, pale yellow needles, resembling glass wool, the m. p., 189°, of which was not further changed by crystallisation. The more soluble fractions were subjected to a prolonged series of fractional crystallisations from alcohol, when stout, pale yellow tablets, m. p. 183°, were obtained. The isolation of these was facilitated by the observation that, after slow crystallisation, they could be partly separated from the filamental needles by shaking and rapidly decanting the mother-liquor, but the process was slow, and after about 40 crystallisations, only 6.0 g. of the needles, m. p. 189°, and 3.1 g. of the tablets, m. p. 183°, had been obtained. Needles, m. p. about 160°, were also obtained, but these appeared to be a difficultly separable mixture of which the needles, m. p. 189°, formed one constituent.

*3-Nitro-ON-diacetyl-o-aminophenol.*—This constitution is assigned to the tablets, m. p. 183° (Found: C, 50.3; H, 4.1.  $C_{10}H_{10}O_5N_2$  requires C, 50.4; H, 4.2%), since the corresponding free phenol is converted by methylation into 3-nitroaceto-*o*-anisidide, the orientation of which is described above. 3-Nitro-*o*-acetylaminophenol was formed as its sodium salt when the acetyl compound (0.5 g.) was treated with 2 c.c. of 2*N*-aqueous sodium hydroxide. The temperature rose to 40° and the solid dissolved, but the deep red solution did not crystallise. The phenol was precipitated on acidification and crystallised from hot water in orange-yellow needles, m. p. 169°.

*4-Nitro-ON-diacetyl-o-aminophenol.*—4-Nitro-*o*-aminophenol (3 g., obtained by reduction of 2:4-dinitrophenol with hydrogen sulphide)

was boiled with acetic anhydride (4.5 g.) and acetic acid (2 g.) for 2 hours. The excess of acetic acid was removed over potassium hydroxide in an evacuated desiccator, and the solid product drained on porous porcelain and crystallised twice from ethyl alcohol, when needles, m. p. 183—184°, were obtained (Found : C, 50.2; H, 4.2.  $C_{10}H_{10}O_5N_2$  requires C, 50.4; H, 4.2%). 4-Nitro-*o*-acetylaminophenol was prepared as in the preceding series, but it yielded an orange sodium salt which separated from the alkaline solution in rosettes of needles. The free phenol crystallised from alcohol in colourless prisms, m. p. 278° (decomp.) (Found : C, 48.8; H, 4.1.  $C_8H_8O_4N_2$  requires C, 49.0; H, 4.1%).

5-Nitro-ON-diacetyl-*o*-aminophenol.—This structure is assigned to the filamental needles, m. p. 189°, obtained by nitration, since the corresponding phenol on methylation gave 5-nitroaceto-*o*-aniside. 5-Nitro-*o*-acetylaminophenol was prepared as in the last case. Crimson needles separated from the alkaline solution, which, on addition of water and acid, yielded the phenol. After crystallisation from ethyl alcohol, this was obtained in small, yellow prisms, m. p. 269° (decomp.) (Found : C, 48.8; H, 4.1.  $C_8H_8O_4N_2$  requires C, 49.0; H, 4.0%).

*Attempted Estimation of the Proportions of 3- and 5-Nitro-derivatives.*—The nitration of diacetylaminophenol (40 g.) was carried out as described above, and the acetic anhydride removed in a vacuum, without separation of the part of the nitration product which crystallised spontaneously, since this was a mixture of isomerides. The solid residue was mixed with 120 c.c. of water and 180 c.c. of 4*N*-aqueous potassium hydroxide, the temperature being kept below 35°. When the decomposition (elimination of the *O*-acetyl group) was completed, the deep red liquid was acidified and the precipitated phenols were collected; a small additional quantity of solid was obtained by extracting the mother-liquor with ether. The whole solid was then mixed with 100 c.c. of 2*N*-potassium hydroxide and shaken at 25—35° with 10 c.c. of methyl sulphate. The methylation was almost complete in an hour, and was finished with the aid of small additional amounts of methyl sulphate and alkali. The precipitated solid was washed with water, boiled for 36 hours with 400 c.c. of 2*N*-aqueous potassium hydroxide (ammonia ceased to be evolved after the first 24 hours), and the cooled product extracted with ether to remove unchanged bases, and basic tars (7.0 g.). After the dissolved ether had been removed in a current of air, the solution was acidified. The mixed guaiacols thus precipitated were kept in contact with the mother-liquor for 24 hours to become thoroughly crystalline, and then collected, the dissolved portions being isolated by extraction with ether (total 25 g.). They

were separated and estimated by steam distillation, as described in the previous example. In this case, owing to the relatively large proportion in which it was present, the *O*-compound crystallised (5.8 g.) in a pure form (orange needles, m. p. 60—61°) from the first 2 l. of distillate. A further 2.2 g. was estimated to be present in solution in the first 3 l. of distillate, by extracting it with pure ether and correcting for the volatility in steam of the *p*-compound with which it was contaminated. Of this 2.2 g., about 1.1 g. were separated in the pure condition by fractional crystallisation from water. The distillate following the first 3 l. contained only the *p*-compound which, without crystallisation, melted at 96—99° and, after crystallisation, at 99—100°. These yields correspond with 23% of 3-nitrodiacetylaminophenol and 48% of the 5-nitro-compound. No solid product could be isolated from the tarry basic fraction, so the quantity of 4- and 6-derivatives formed is left undetermined.

### (III) Nitration of *N*-Methylaceto-*o*-Anisidide.

*N*-Methyl-*o*-anisidine was prepared by methylating the formyl derivative of *o*-anisidine and, after hydrolysis of the formyl group, was isolated by means of the nitrosoamine, which was reduced to the secondary base as described by Diepolder (*Ber.*, 1899, 32, 3515).

*N*-Methylaceto-*o*-anisidide was prepared by boiling the base for 2 hours with a slight excess of acetic anhydride and distilling the product. The fraction, b. p. 158—160°, set on cooling to a mass of large, inclined prisms, m. p. 46—50°, which, after crystallisation from ether-ligroin, melted at 51—53° (Found: C, 67.4; H, 7.3.  $C_{10}H_{13}O_2N$  requires C, 67.0; H, 7.3%).

*Mononitration: Isolation of 5-Nitro-, 4-Nitro-, and 3- or 6-Nitro-derivatives.*—A cooled mixture of fuming nitric acid (2.5 c.c.) and acetic anhydride (12 c.c.) was added to *N*-methylaceto-*o*-anisidide (10 g.) dissolved in acetic anhydride (24 c.c.), the temperature being kept below 35°. Two methods of isolating the crude nitration product were employed. (i) The solution was poured into water, shaken to decompose the acetic anhydride, and made alkaline with sodium carbonate. Any solid which separated was collected, and the filtrate extracted with ether. The extract was dried with calcium chloride and reduced by evaporation to a small bulk, the crystals being separated fractionally. (ii) The acetic anhydride was removed by evaporation in a vacuum over potassium hydroxide.

Methylaceto-*o*-anisidide (20 g.) on nitration, followed by treatment in accordance with method (i), yielded 12.5 g. of a crystalline solid, m. p. 117—119°, which on crystallisation from ether formed

pale yellow prisms, m. p. 119—120.5°. This was shown to be 5-nitro-*N*-methylaceto-*o*-anisidide by direct comparison with a specimen synthesised as described below (Found : C, 53.8; H, 5.4.  $C_{10}H_{12}O_4N_2$  requires C, 53.6; H, 5.4%).

On evaporating the ethereal extract to small bulk, very pale yellow prisms, m. p. 120—125°, which depressed the m. p. of the 5-nitro-compound, separated (0.9 g.). On crystallisation from benzene-ligroin the m. p. was raised to 126.5—127.5°. This substance was identified as 4-nitro-*N*-methylaceto-*o*-anisidide by comparison with a specimen synthesised as described below (Found : C, 53.8; H, 5.4; N, 12.7.  $C_{10}H_{12}O_4N_2$  requires C, 53.6; H, 5.4; N, 12.5%).

The ethereal solution from which this had separated, on cooling to -15°, deposited crystals (1.6 g.), m. p. 98—99°, from which 0.65 g. of pure 5-nitro-compound was separated by fractional crystallisation. The second substance present in this fraction could not be definitely identified.

On long standing, the residual ethereal solution deposited large, colourless prisms, m. p. 103—105°, which after crystallisation from ether melted at 105—106° (0.08 g.). This m. p. was not changed by further crystallisation (Found : C, 53.6; H, 5.3.  $C_{10}H_{12}O_4N_2$  requires C, 53.6; H, 5.4%). We believe this substance to be 3-nitro-*N*-methylaceto-*o*-anisidide, which is certainly formed in the nitration (see below), but there is no definite proof that it is not the 6-nitro-isomeride. A further quantity of these crystals (0.16 g.) separated after a few weeks, but the remainder of the nitration product refused to crystallise. The compound, m. p. 105—106°, yielded on hydrolysis a base melting at about the ordinary temperature, but the quantity obtained was too small for purification. In another nitration carried out as far as possible under similar conditions, none of the above nitro-compound was isolated, only the 4-derivative, m. p. 126.5—127.5°, being obtained on cooling the ethereal solution to -20°.

Preliminary experiments having shown that 5-nitro-*N*-methylaceto-*o*-anisidide only slowly evolves methylamine on boiling with 2*N*-alkali, but that this reaction occurs at 120° in sealed tubes (although not so smoothly as the analogous reaction described previously), the presence of 3-nitro-*N*-methylaceto-*o*-anisidide was proved by the following experiment. *N*-Methylaceto-*o*-anisidide (7.3 g.) was nitrated in the usual way, and the product treated in accordance with method (ii). The crude product (8.7 g.; theory 9.0 g.) having partly crystallised (4.3 g. of the 5-nitro-derivative), a portion (3.4 g.) of the mechanically separated oil was heated with 30 c.c. of 2*N*-aqueous potassium hydroxide for 12.5 hours at 120°.



After extraction of the basic portion \* (1.0 g.) with ether, the solution was acidified and the guaiacols (1.8 g.) were extracted. Fractional distillation in steam indicated the presence of 0.29 g. of 3-nitroguaiacol, and a small portion of this was obtained from the early fractions of the steam distillate; after crystallisation from water, it was identified by comparison and a mixed m. p. determination with the specimen obtained as described previously.

*5-Nitro-N-methyl-o-anisidine*.—The acetyl derivative (above) (0.9 g.) was heated with concentrated hydrochloric acid for 1.5 hours on the steam-bath, and the reaction completed by boiling for 45 minutes. Neutralisation with ammonia precipitated the base, which separated from methyl alcohol or light petroleum in long, bright yellow, flattened needles, m. p. 101–102°. It was identified as 5-nitro-*N*-methyl-*o*-anisidine by comparison with a specimen prepared by synthesis (below) (Found: C, 52.6; H, 5.4.  $C_8H_{10}O_3N$  requires C, 52.7; H, 5.5%).

*4-Nitro-N-methyl-o-anisidine*.—Prepared in the same way from its acetyl derivative (above), this base separated from light petroleum in orange, hair-like crystals, m. p. 87°, which were identified by comparison with a synthesised specimen (below) (Found: C, 52.6; H, 5.5.  $C_8H_{10}O_3N_2$  requires C, 52.7; H, 5.5%).

*Synthesis of 5-Nitro-N-methyl-o-anisidine*.—5-Nitroanisidine (1 g.), methyl iodide (0.9 g.), and methyl alcohol (2 c.c.) were heated together for 1.5 hours at 100° in a sealed tube. The alcohol was then evaporated, and dilute potassium hydroxide was added to precipitate the bases which, after partial purification with chloroform, yielded the secondary base on crystallisation from dilute methyl alcohol and from light petroleum.

*Synthesis of 4-Nitro-N-methylaceto-o-anisidine and 4-Nitro-NN-dimethyl-o-anisidine, 4-Nitro-N-methyl-o-anisidine, and 4-Nitro-3(or 5)-methylaceto-o-anisidine*.—4-Nitroanisidine (6 g.), methyl iodide (5.4 g.), and methyl alcohol (12 c.c.) were heated for 2 hours at 100°, and the mixture of bases was isolated, as in the previous preparation. Many attempts were made to separate these by fractional crystallisation, but without success, and the mixture was therefore heated with acetic anhydride for 45 hours. After the excess of this reagent had been evaporated, water was added and the mixture made alkaline with sodium carbonate and extracted with ether, the extract

\* As in the two cases previously described, the bases recovered after alkali treatment contained products of some more complex change than the mere elimination of an acetyl group from the 4- or 6-nitro-derivative. In this experiment, the basic fraction, even after distillation and attempted acetylation, yielded liquids which could not be crystallised and the nature of which was not revealed by analysis.

being washed with 15% hydrochloric acid. This was intended to remove the tertiary base from the mixture of acetyl compounds of the primary and secondary bases, and in the earlier experiments by this method 4-nitro-*NN*-dimethyl-*o*-anisidine was isolated in this way, the material obtained by basifying the hydrochloric acid solution and extraction with ether setting to a solid mass, which, on crystallisation from ligroin, yielded bright yellow, short needles, m. p. 38—39.5° (Found: C, 54.7; H, 6.0.  $C_9H_{12}O_3N_2$  requires C, 55.1; H, 6.1%).

In certain subsequent experiments, carried out as far as possible under the same conditions, the bases obtained from the hydrochloric acid extract did not solidify immediately, but on keeping for several weeks in an evacuated desiccator, partly crystallised. The crystals thus obtained separated from benzene-ligroin in very pale yellow prisms, m. p. 127—128°, which did not depress the m. p. of the specimen of 4-nitro-*N*-methylaceto-*o*-anisidine obtained by nitration. On hydrolysis with hydrochloric acid, the substance yielded 4-nitro-*N*-methyl-*o*-anisidine, m. p. 87°, which was similarly identified with the base prepared from the 4-nitration product. As an isomeric base, in which the methyl group has apparently migrated to the ring, was also isolated in the course of these experiments (see below), the secondary character of this base, m. p. 87°, was confirmed by the preparation of its *nitrosoamine*, which was precipitated at once when sodium nitrite was added to a solution of the hydrochloride. Crystallised from benzene-ligroin, this compound formed very pale yellow needles, m. p. 119—120° (Found: N, 20.3.  $C_8H_9O_4N_3$  requires N, 19.9%). From these experiments, it must be concluded that 4-nitro-*N*-methylaceto-*o*-anisidine is fairly easily soluble in hydrochloric acid of the strength used. The oil from which the crystals of this compound were obtained set, some weeks later, to a solid mass consisting principally of the tertiary base described above.

The ethereal solution from which the above-mentioned substances were extracted by hydrochloric acid, on evaporation, yielded a solid residue which examination with a lens showed to contain at least two compounds. One of these was easily separated by fractional crystallisation and proved to be the acetyl derivative of the original primary base. The second compound was separated partly by crystallisation and partly mechanically, and, after a final crystallisation from benzene-ligroin, was obtained as pearly plates, m. p. 127—128°. It therefore had the same m. p. as 4-nitro-*N*-methylaceto-*o*-anisidine, but its crystalline form was entirely different, and a mixture of the two compounds melted at about 100°. Analysis showed the new compound to be an isomeride (Found: C, 53.2; H, 5.1; N, 12.2.  $C_{10}H_{12}O_4N_2$  requires C, 53.6; H, 5.4; N, 12.5%),

and it must therefore be 4-nitro-3(or 5)-methylaceto-o-anisidide, a methyl group having wandered to the ring. To confirm this, the compound was boiled with hydrochloric acid for 0.5 hour to eliminate the acetyl group, and the hydrochloride of the base diazotised in the usual way. No precipitate separated, indicating that secondary bases were absent, but on pouring the product into alkaline  $\beta$ -naphthol solution, a deep crimson dye was immediately precipitated.

*Action of Methyl Iodide on 6-Nitro-o-anisidine.*—The base (2.2 g.), methyl iodide (2.0 g.), and methyl alcohol (4.5 c.c.) were heated together, and the products treated as in the methylation of 4-nitro-anisidine. The mixture of acetyl compounds only partly solidified after long keeping. After several crystallisations from ether, colourless prisms were obtained, m. p. 106–107°, which depressed the m. p., 103–104°, of 6-nitroaceto-o-anisidide (Found: C, 52.7; H, 5.2.  $C_8H_{10}O_3N_2$  requires C, 52.7; H, 5.5%). These analytical figures agree moderately well with those required for a nitromethylanisidine, but as the crystals were colourless, whilst the nitromethylanisidines described above are orange or yellow, it seems unlikely that this compound is a nitro-base of the series. Owing to the limited quantity of 6-nitro-o-anisidine available, we were not able to make a more detailed study of its methylation products, or to carry out further experiments with the substance described.

*Attempted Estimation of the Proportions of the Nitration Products.*—

(a) *N*-Methylaceto-o-anisidide (20 g.), nitrated as described above and treated by method (ii), gave 11.8 g. of crystalline 5-nitro-derivative and 12.0 g. of an oily mixture (total 23.8 g.; theory 25.0 g.). A part of the oil (9.3 g.) gave guaiacols consisting, as estimated from fractional distillation in steam, of 3.3 g. of 5-nitro- and 1.0 g. of 3-nitro-guaiacol. A basic oil (2.7 g.) and a neutral tar (1.0 g.) were also obtained.

(b) In another experiment, 20 g. of *N*-methylaceto-o-anisidide yielded 14.0 g. of the 5-nitro-derivative and 0.9 g. of the 4-nitro-derivative, both isolated as such in the pure condition. In another experiment, in which the material was treated by method (i), similar quantities of the 5- and 4-nitro-compounds were isolated, and also 0.24 g. of an isomeride believed to be the 3-nitro-derivative.

Combining these results, 73% of the material is accounted for as follows: 5-nitro-derivative, 64%; 4-nitro-derivative, 4%; 3-nitro-derivative, 5%.

*Addendum.* ON-Diacetyl-*N*-methyl-o-aminophenol.—*N*-Methyl-o-aminophenol, which we found to melt at 88° instead of 80° as recorded in the literature, (44 g.) was boiled for 1 hour with acetic anhydride (70 c.c.), and the product distilled. The fraction, b. p. 160–170°/2 mm., at once solidified to crystals (61 g., m. p. 58–60°) which, after

crystallisation from ether-ligroin, had m. p. 63—64° (Found : C, 64.0; H, 6.2.  $C_{11}H_{13}O_3N$  requires C, 63.8; H, 6.3%).

Originally it was intended to include a study of the nitration of this substance in this investigation, but this project was abandoned when it was found that a considerable amount of oxidation took place under the conditions which had been used for the mononitration of the other three substances.

We wish to thank the Royal Society for a grant with the aid of which part of the expense of this investigation has been met.

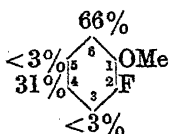
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# CLXX.—*The Nature of the Alternating Effect in Carbon Chains. Part VI. A Study of the Relative Directive Efficiencies of Oxygen and Fluorine in Aromatic Substitution.*

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IN continuation of the work, described in the preceding part, on the establishment of the sequence  $N > O > F$  for the *op*-directive powers of these atoms in the neutral state and directly attached to the benzene ring, the method previously used for comparing the relative directive efficiencies of nitrogen and oxygen atoms has now been applied to the comparison of oxygen with fluorine. *o*-Fluoroanisole has been nitrated with the results indicated in the following formula :



The methods by which these figures have been determined are fully described in the experimental portion, and it need only be stated here that the 3- and 5-nitro-derivatives were estimated together (2.7%) by taking advantage of the lability of their fluorine towards alkaline reagents, and that the 4-nitro-compound was estimated colorimetrically after reduction, utilising the fact that *p*-anisidine gives a violet coloration with ferric chloride, whilst the *o*-compound does not. The 4-nitro-derivative was isolated as such from the nitration mixture and identified by synthesis, whilst the 6-nitro-compound, which was also synthesised and was a liquid at

the ordinary temperature, was reduced with elimination of fluorine and identified as *o*-anisidine hydrochloride.

From the data given, it is clear that whether we disregard the large amount of *o*-substitution as an effect to which special influences contribute and consider only substitution in positions 4 and 5, or whether we accept the total *op*-direction by each group as the better measure of its directive power, the oxygen atom is the more effective directing agent. So great is the difference that although only one case has been investigated it appears reasonable to infer that the conclusion drawn will hold generally amongst derivatives of *o*-fluorophenol.

The sequence  $N > O > F$  is thus established; and this is the expected sequence, since the electronic grouping of fluorine most closely approaches the internally satisfied condition exemplified in neon (preceding paper).

#### EXPERIMENTAL.

*Preparation of o-Fluoroanisole.*—Some difficulty was experienced in obtaining this substance, but it was ultimately prepared by the action of hydrofluoric acid on the *diazopiperidide* obtained from *o*-anisidine. A solution of 25 g. of *o*-anisidine in 60 c.c. of hydrochloric acid was diazotised below  $0^\circ$  by a solution of 15 g. of sodium nitrite in 50 c.c. of water, the mixture being mechanically stirred. On pouring the product into a solution of potassium hydroxide (30 g.) and piperidine (17 g.) in 150 c.c. of water, an oil was precipitated which rapidly solidified (yield 35–37 g.) and on crystallisation from methyl alcohol yielded lemon-yellow prisms, m. p.  $30^\circ$  (Found: C, 65.0; \* H, 7.6.  $C_{12}H_{17}ON_3$  requires C, 65.8; H, 7.8%).

This *diazopiperidide* (35 g.) was heated for 1 hour on the steam-bath with 150 c.c. of concentrated aqueous hydrofluoric acid. Ice was then added and the mixture poured into an excess of 30% aqueous sodium hydroxide, care being taken to avoid over-heating, since the fluoroanisole is very volatile with steam. The *fluoroanisole* was isolated by distillation in steam and separated from the piperidine contained in the steam-distillate by extraction with ether after acidification. It is a colourless, mobile liquid, b. p.  $154$ – $155^\circ$  (Found: C, 66.6; H, 5.6.  $C_7H_7OF$  requires C, 66.7; H, 5.6%). The average yield was 6% of the theoretical.

*Dinitration.*—In a preliminary experiment in which 1 g. of *o*-fluoroanisole was run through a fine capillary tube into 2 c.c. of

\* A better analysis is, unfortunately, not available; difficulty was experienced in burning the substance owing to the rapidity with which it decomposed.

nitric acid ( $d$  1.5) at  $-10^{\circ}$ , and the product mixed with crushed ice, a solid dinitro-compound was obtained which on crystallisation from ethyl alcohol formed pale yellow needles, m. p.  $86-87^{\circ}$ . Judging from the results of mononitration (below), we believe this to be 4:6-dinitro-2-fluoroanisole, although no special proof of its constitution is here offered (Found: C, 38.7; H, 2.2.  $C_7H_5O_5N_2F$  requires C, 38.9; H, 2.3%).

*Mononitration.*—*o*-Fluoroanisole (6.5 g.), mixed with acetic anhydride (25 g.), was treated at  $0^{\circ}$  with a mixture of fuming nitric acid (2.20 c.c.) and acetic anhydride (9 c.c.). The nitration proceeded smoothly with evolution of heat, and the mixture was kept at the ordinary temperature for 3–4 hours and then poured into water. The oil which separated was collected and diluted with ether, the aqueous solution was extracted with ether, and the combined ethereal solutions were dried and evaporated. The residue, after drying for a short time over potassium hydroxide, was distilled, practically the whole boiling at  $114-116^{\circ}/2$  mm. (Found: C, 49.2; H, 3.4.  $C_7H_6O_3NF$  requires C, 49.1; H, 3.5%).

*3-Nitro- and 5-Nitro-o-fluoroanisole.*—These were estimated together by taking advantage of the lability of their fluorine in the presence of boiling 0.5*N*-aqueous sodium carbonate, or dilute methyl-alcoholic sodium methoxide prepared from 2 g. of sodium and 200 c.c. of methyl alcohol. With the first of these reagents at its boiling point, and with the second at  $60^{\circ}$ , a quantity of fluoride ion corresponding with the decomposition of about 2.5–3.0% of nitrofluoroanisole was liberated rapidly, whilst prolonged treatment produced very little further action. After 3 hours' treatment with boiling sodium carbonate, the liberation of fluoride ion corresponded to 2.7% of decomposed nitrofluoroanisole (average of three concordant determinations) and almost the same figure, 2.8%, was obtained on using sodium methoxide. To ascertain if any correction was needed for the possible decomposition of the 4- and 6-nitro-derivatives, these two substances (see below) were treated for the same period under the same conditions. With 4-nitrofluoroanisole and sodium carbonate, the decomposition was zero (two determinations), and the same result was obtained with sodium ethoxide. Only a small quantity of 6-nitrofluoroanisole was available, but a single determination by the sodium carbonate method indicated the decomposition of 0.2%. From these results it is evident that the 4- and 6-nitro-derivatives do not decompose appreciably under the conditions used. On the other hand, 4-nitrofluoroanisole is decomposed at a measurable velocity at  $85^{\circ}$  by sodium methoxide of the dilution stated above, and, in this connexion, reference may be made to Holleman and Beekman's experiment on the alcoholysis of

*m*-nitrofluorobenzene (*Rec. trav. chim.*, 1904, 23, 235). The mixed 3- and 5-nitroguaiacols were isolated from the above decompositions with sodium, but the quantity was too small for the estimation of their relative proportions by the steam distillation method employed by Ingold and Ingold (preceding paper). A small quantity of pure 5-nitroguaiacol was isolated by taking advantage of the sparing solubility of its potassium salt in 4*N*-aqueous potassium hydroxide.

4-Nitro-*o*-fluoroanisole.—The nitrofluoroanisoles recovered after decomposition of the 3- and 5-derivatives with sodium carbonate formed a mixture which was liquid at the ordinary temperature but, on cooling in an efficient freezing mixture, set to a paste of crystals. These were collected below  $-20^{\circ}$ , and when freed from adhering oil, had m. p.  $47-49^{\circ}$ . By crystallisation from ligroin pale yellow prisms were obtained, m. p.  $52-52.5^{\circ}$ , which were identified by direct comparison and a mixed m. p. determination with a specimen synthesised as described below. The yield accounted for about 10% of the nitration product.

*Synthesis of 4-Nitro-*o*-fluoroanisole.*—4-Nitro-*o*-anisidine (25 g.) prepared from 2:4-dinitrochlorobenzene, *via* 2:4-dinitroanisole, was dissolved in 50 c.c. of boiling 20% hydrochloric acid, and the solution cooled with rapid stirring to ensure fine division of the solid. Diazotisation was effected in the usual way with 11 g. of sodium nitrite, and the mixture poured into a solution of 30 g. of potassium hydroxide and 13 g. of piperidine in 150 c.c. of water with the addition of sufficient ice to maintain the temperature at  $0^{\circ}$ . The oily precipitate soon solidified (yield, 35 g.), and crystallisation from ethyl alcohol gave buff needles, m. p.  $95-96^{\circ}$  (Found: C, 54.5; H, 6.0.  $C_{12}H_{16}O_3N_4$  requires C, 54.2; H, 5.9%). This *diazopiperidide* (35 g.) was warmed on the steam-bath for 1 hour with 175 c.c. of concentrated hydrofluoric acid, the mixture being rapidly stirred at the commencement of the process. After the addition of ice the mixture was poured into 1.5 l. of 30% sodium hydroxide kept at  $0^{\circ}$ , and after complete neutralisation the mixture, which contained a brown precipitate of unknown constitution, was distilled in a current of steam. The nitrofluoroanisole crystallised in the receiver, but it was found convenient to extract it with ether. It melted at  $45-49^{\circ}$  in the crude condition and at  $52-53^{\circ}$  after crystallisation from ligroin (Found: C, 49.3; H, 3.5.  $C_7H_6O_3NF$  requires C, 49.1; H, 3.5%). The yield was 1.3 g., that is, 7% of the theoretical.

On reduction by boiling for 15 minutes with stannous chloride and hydrochloric acid it was converted smoothly into *p*-anisidine, the elimination of fluorine being quantitative. The anisidine thus obtained melted at  $56-57^{\circ}$ , alone and when mixed with a genuine specimen (Found: C, 68.8; H, 7.5. Calc.: C, 68.9; H, 7.4%).

Calc. for  $C_7H_8ONF$ : C, 59.6; H, 5.7%). An application of this reaction is described below.

*Synthesis of 6-Nitro-o-fluoroanisole.*—The silver salt of 2:6-dinitrophenol was boiled with a benzene solution of methyl iodide, and the dinitroanisole so obtained was reduced by hydrogen sulphide in methyl-alcoholic ammonia solution to 6-nitro-*o*-anisidine (yield 35%). The *hydrochloride* of this base separated from hydrochloric acid in clusters of pale yellow needles, m. p. 198°.

The base was converted into its *diazopiperidide* by the method described in the preceding paragraph. The *diazopiperidide*, after draining on porous porcelain, but without further purification, was decomposed with hydrofluoric acid, and the 6-nitro-*o*-fluoroanisole isolated by distillation in steam. After redistillation it was obtained as a pale yellow oil, b. p. 110°/1 mm. (Found: C, 49.6; H, 3.7.  $C_7H_8O_3NF$  requires C, 49.1; H, 3.5%).

On reduction by stannous chloride and hydrochloric acid *o*-anisidine was obtained unaccompanied by any fluoro-base.

*Estimation of the Proportions of 4- and 6-Nitro-o-fluoroanisoles obtained by Nitration.*—The mixture of 4- and 6-nitrofluoroanisoles obtained after decomposition of the 3- and 5-nitro-isomerides by sodium carbonate was reduced with stannous chloride as described above. The yield of distilled bases was 90% of the theoretical, and analysis showed that the whole of the fluorine had been eliminated (Found: C, 69.1; H, 7.2%).

A weighed portion of these mixed bases was treated with hydrochloric acid; *o*-anisidine hydrochloride (m. p. 225°, alone and mixed with an authentic specimen; a mixture with *p*-anisidine hydrochloride, m. p. 215°, melted at 170–180°) was thus obtained. The yield corresponded with 48% of 6-nitrofluoroanisole in the original mixture.

In order to estimate the relative proportions of *o*- and *p*-anisidine in the mixture of these bases, a series of artificial mixtures, in the proportions 20 : 80, 40 : 60, 60 : 40, and 80 : 20, was prepared in the form of 1% solutions in ethyl alcohol. Each of these was tested in turn against a 1% solution of the experimental mixture, equal volumes of the solutions under comparison being added to equal portions of a solution of ferric chloride in similar colorimeter tubes. By comparing the colours, it was found that the proportion of *p*-isomeride in the experimental mixture lay between 20% and 40%. The process was repeated with three more standards, containing 25%, 30%, and 35%, respectively, of *p*-compound. As these tests indicated that the proportion of *p*-isomeride lay between 30% and 35%, an additional standard, containing 32.5% of *p*-anisidine and 67.5% of *o*-anisidine, was made. This agreed as exactly as could be



ascertained with the experimental mixture, both as regards rate of development of the colour and its maximum intensity. The conditions being so adjusted that about 2—4 minutes were required for the colour to reach its maximum intensity, it was found that the rate of development of colour was more sensitive than maximum intensity to changes of composition and served as a better means of comparison. In the final experiments, therefore, all solutions were immersed in the same bath before mixing, and to avoid differences of temperature during the readings the two tubes were surrounded by a metal screen and symmetrically illuminated. The results are believed to be correct to 2%.

On acetylation of the experimental mixture of bases, a mixture of acetyl derivatives was obtained which set at 59°, and admixture with small amounts of either aceto-*o*-anisidide or aceto-*p*-anisidide raised this setting point, whence it appears that the proportion in which the two substances were present in the acetylation product corresponds approximately with the eutectic composition. The following approximate setting points of mixtures of aceto-*o*-anisidide and aceto-*p*-anisidide indicate that the eutectic contains about 31% of the *p*-compound and sets at 60°, and this supplies confirmation of the figure obtained colorimetrically :

Proportion of para- ...	17.3%	21.4%	24.4%	30.6%	35.0%	39.1%
Setting point .....	71°	67.5°	64°	60°	63.5°	67°

These values were determined by the cooling curve method.

We wish to thank the Chemical Society and the Royal Society for grants with the aid of which the expenses of this investigation have been met.

THE UNIVERSITY, LEEDS.

[Received, February 10th, 1926.]

## CLXXI.—*A Method for Determining the Solubility of Sparingly Soluble Substances.*

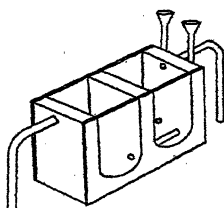
By STOTHERD MITCHELL.

THE methods available for determining the solubility of sparingly soluble substances are of limited application. Electrical measurements are restricted to electrolytes, and chemical analysis is useful for only a few substances. The optical method now described can, however, be employed more generally.

For this work, an interferometer of the type described by Jamin (*Ann. Chim. Phys.*, 1858, 52, 171) was constructed. Mercury green

light ( $\lambda = 5461$ ) was used throughout as the source of illumination. A special form of double cell was required in which liquids could be circulated through each compartment (Fig. 1). It was cut from a rectangular block of brass (2.5 cm. broad), and was fitted with inlet and outlet tubes of the same metal. The sides were made of the best quality optical glass cemented in position. Both compartments of the cell were first filled with water, and the compensator was adjusted so that the cross wires of the observing telescope coincided with one of the interference bands. When a dilute aqueous solution was gradually allowed to displace the water in one half of the cell, there was a movement of the bands. By means of a fine adjustment on the compensator the same band could be kept on the telescope cross wires.

FIG. 1.



Over the range considered, the compensator readings increased in proportion to the number of bands displaced, and therefore to the difference in refractive index between

the contents of the two compartments of the cell (Table I).

TABLE I.

Bands.	0.	2.	4.	6.	8.	10.	12.	14.	16.	18.	20.
Compensator readings ...	10	13.6	17.0	20.5	24.0	27.7	31.5	35.0	39.0	43.0	46.5

As a preliminary it was necessary to investigate the nature of the curves correlating compensator readings and concentration. To do this, a number of saturated solutions of substances slightly soluble in water were prepared at room temperature. A series of dilutions of each was made, and these together with a quantity of water were allowed to stand until all were at the same temperature. Both divisions of the cell were then filled with water, and the zero-reading was taken. Water was allowed to circulate through one compartment, and the most dilute solution through the other. When no further movement of the bands took place, the reading was noted. The next solution was then allowed to displace the more dilute, and so on till the saturated solution was reached. A number of results are shown in Table II and Fig. 2. All substances so far investigated give straight lines with the exception of benzene. In view of this exception, it will always be necessary to plot a graph of % *saturation* against *compensator readings* as a preliminary to a solubility determination by this method. When the graph is a straight line, only one weighing is necessary to calibrate the concentration scale, and if the reading for the saturated solution is

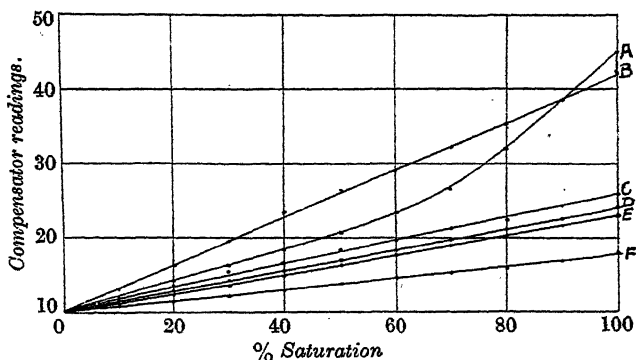
TABLE II.

Compensator readings for % saturation.

Substance.	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	100.
Benzene .....	10.0	12.0	14.3	16.2	18.5	20.8	23.5	26.5	32.0	38.5	45.0
Camphor .....	10.0	12.8	16.3	19.8	23.6	26.7	29.0	32.2	35.6	38.7	43.2
sec.-Octyl alcohol	10.0	12.4	14.0	15.5	16.8	18.8	20.0	21.5	22.4	24.5	26.0
Borneol .....	10.0	11.5	12.8	14.1	15.3	16.7	18.3	19.4	20.8	22.3	24.0
Methyl salicylate .....	10.0	11.0	12.2	13.5	15.0	16.4	17.9	19.1	20.3	21.6	23.0
Naphthalene.....	10.0	11.0	11.5	12.0	12.6	13.7	14.3	14.8	15.5	16.8	18.1

determined the weight of the solute present in it can be found graphically by extrapolation. In practice, it is advisable to prepare one or more dilutions from the solution of known concentration so that there may be a gradual movement of the bands without

FIG. 2.



A. Benzene. B. Camphor. C. sec.-Octyl alcohol. D. Borneol.  
E. Methyl salicylate. F. Naphthalene.

blurring. Should the graph not be a straight line, a number of weighings would be necessary and the method would lose its merit of simplicity.

When a solubility is required at a temperature other than room temperature, a saturated solution is prepared at that temperature and separated off; then, if necessary, a known quantity of water is added so that the solute will remain completely in solution at the temperature of the room in which the readings are taken. The saturated solutions were prepared in stoppered bottles which were rotated in a thermostat with excess of solute for several hours at the required temperature. Table III shows a number of results.

As an indication of the accuracy with which these results could be reproduced, it may be mentioned that a duplicate determination with lead sulphate gave the same value as shown, *i.e.*, 0.032 at 15°,

TABLE III.

[In each case, Solution A<sub>1</sub> was made up as shown in column 2, and Solution A<sub>2</sub> was a two-fold dilution of A<sub>1</sub>. These were used for the standardisation, by means of which the concentrations of B<sub>1</sub> (saturated) and B<sub>2</sub> (half-saturated) were deduced from their compensator readings.]

Substance.	G. of substance in 1000 c.c. of water.	Compensator readings.				Temp. of water).	Solubility (g. per 1000 c.c.
		Soln. A <sub>1</sub> .	Soln. A <sub>2</sub> .	Soln. B <sub>1</sub> .	Soln. B <sub>2</sub> .		
Naphthalene ...	0.0200	14.0	12.0	14.5		15°	0.022
					14.0	25	0.040
Lead sulphate	0.0250	11.4	10.7	11.8		15	0.032
Borneol .....	0.5000	18.3	14.3	21.4		15	0.693
					16.2	25	0.740
sec.-Octyl alcohol	1.0407	19.0	14.5	23.5		15	1.508
				21.5		25	1.280

and two additional experiments with borneol gave the following results: 0.697, 0.697 at 15°; 0.740, 0.734 at 25°.

Water has been used as solvent in these experiments, but the method could be extended to other solvents if they are not too volatile.

The author desires to thank Miss Janet M. Henderson for assistance with the experimental work.

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## CLXXII.—*The Inhibition of the Glow of Phosphorus.*

By HARRY JULIUS EMELEUS.

THE slow luminous oxidation of phosphorus is influenced by the addition of a gas or vapour in one of two ways. Gases such as hydrogen, nitrogen, and carbon dioxide effect a dilution, and the kinetics of the reaction continue to obey the law of mass action. In other cases, however, (e.g., many organic vapours) a small concentration of the added substance stops the reaction and the accompanying phenomena of ionisation and formation of ozone. Phosphorus has, moreover, the remarkable property of oxidising much more slowly, and without luminescence, in pure oxygen when the partial pressure of this gas exceeds a limiting value determined by the temperature. The existence of such a pressure is readily demonstrated by gradually evacuating a vessel containing phosphorus and oxygen. At atmospheric pressure, the reaction is imperceptible, but when the "glow pressure" is reached the phosphorus surface lights up suddenly as the normal oxidation begins. Apparently in this case the oxidation is inhibited by oxygen itself.

Various suggestions have been made to account for these anomalies. One of the earliest was that the ozone formed during the reaction was an essential catalyst, and that it was destroyed by the poisons (Schönbein, *J. pr. Chem.*, 1845, **36**, 246). It is remarkable how often such a reaction is found to be possible. For example, turpentine, ethylene, and benzene can all act as inhibitors, and all react readily with ozone, yet in other cases any such action is very much feebler. Qualitative tests were made to examine the action of ozone on acetone, methyl ethyl ketone, hexane, chlorobenzene, and ethyl iodide. The first three gave definite evidence of a slow reaction, whilst the last two were more readily attacked. It is evidently wrong to assert that any of these substances is quite inert. If this were the true explanation of inhibition, however, the relative activity of different poisons would presumably be that of their reactivity towards ozone, and in some cases this is not so; e.g., acetone is a stronger poison than benzene, but is less readily attacked by ozone.

The alternative suggestion that poisons form protective surface films on the solid phosphorus is unlikely, for Centnerszwer has shown that phosphorus exerts its normal vapour pressure in presence of inhibitors (*Z. physikal. Chem.*, 1913, **85**, 99).

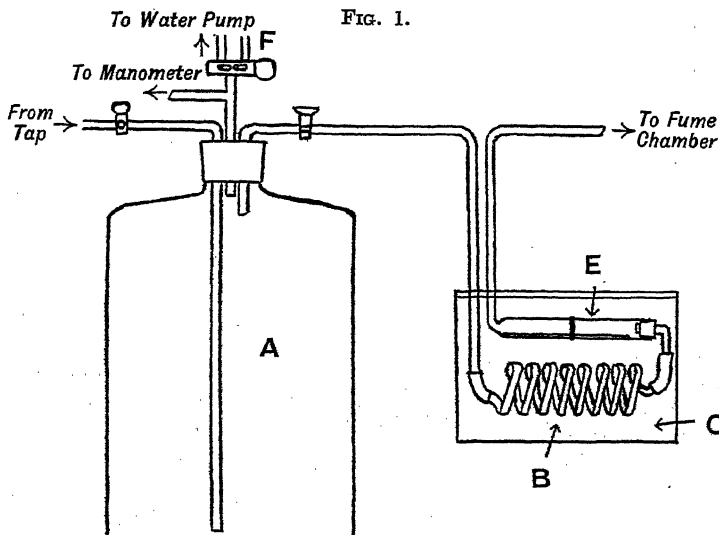
The view now generally held is that the propagation of the glow is a process analogous to the passage of a flame through a combustible gas mixture, and that poisons prevent this from occurring. Lord Rayleigh has, in fact, shown that this is probably correct in the particular case of inhibition by excess of oxygen (*Proc. Roy. Soc.*, 1923, *A*, **104**, 322). Extending the earlier experiments of Bloch (*Compt. rend.*, 1908, **147**, 842), he measured the blast of gas necessary to blow the glow from a given phosphorus surface in various oxygen-nitrogen mixtures, and found that it became less as the percentage of oxygen was increased. Assuming that the blast required to maintain the glow in a stationary position downstream is a measure of the virtual rate of propagation upstream, it follows that successive increases in the oxygen concentration decrease the rate of propagation.

The position of oxygen is unique, since it both supports and inhibits combustion, and it cannot be assumed *a priori* that the more active poisons act in the same way. In the experiments to be described, this point has been studied by applying Lord Rayleigh's method of investigation to the propagation of the glow in presence of the strong inhibitors ethylene, benzene, chloroform, and aniline, and results similar to those for oxygen have been obtained.

*The Propagation of the Glow of Phosphorus in the Presence of Inhibiting Substances.*

The phosphorus used throughout was purified by an acid dichromate solution, as described by Downey (J., 1924, 125, 347). Oxygen was obtained from a cylinder.

The apparatus consisted of a large bottle, A (Fig. 1), into which water was run from the tap. The gas stream so produced was passed through the metal coil, B, where it attained the temperature of the bath, C, and then over a flat phosphorus surface cast in the cylindrical tube, E (14 cm. long, 1 cm. internal diameter). Round



E, about half-way along, a narrow black band was fixed, and in all the experiments the gas stream was adjusted so as to blow the glow from the phosphorus surface up to this mark. From a direct measurement of the rate at which water was flowing into A, the velocity of the blast through E could be calculated.

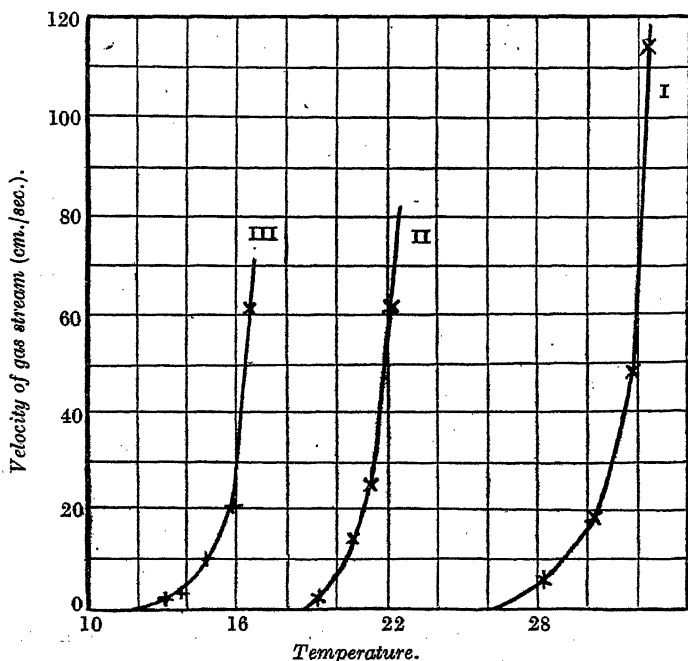
*Dependence of the Blast upon the Percentage of Ethylene added to the Air.*—To obtain the low concentrations of ethylene (less than 0.5%), a mixture of ethylene and air in known proportions was prepared in a gas holder connected to F (Fig. 1). A was then evacuated, and the ethylene-air mixture and air were admitted in the desired proportions as indicated by the mercury manometer. The solubility of the ethylene in the water during the short time of contact was neglected as being within the limits of experimental error. The same phosphorus surface was used throughout. Measurements of the

gas stream needed to blow the glow to the mark were made for different ethylene concentrations at a temperature of 20°. In this way, a series of relative values was obtained, showing the influence of the admixed gas on the propagation of the glow:

Velocity of gas stream (cm./sec.)	140	31	24	17	8	1	1
% Ethylene (by volume) .....	0.16	0.26	0.28	0.36	0.38	0.43	0.46

With less than 0.15% of ethylene the greatest gas stream obtainable was insufficient to blow the glow off the phosphorus surface. As the

FIG. 2.



Air saturated (I) with benzene; (II) with chloroform; (III) with aniline.

ethylene concentration was increased it became easier to blow the glow away, and complete inhibition occurred at a concentration of 0.45%.

*Dependence of the Blast upon the Temperature, in the Presence of a Constant Concentration of Inhibiting Substance.*—Three typical poisons, benzene, chloroform, and aniline, were introduced in large excess into A (Fig. 1) in successive series of experiments, and the air was allowed to become saturated with the vapour at room temperature (16°). The blast of saturated gas which just sufficed to clear the phosphorus surface of luminosity was then determined as

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already described for various temperatures of the bath, C. The results are reproduced in Fig. 2. In each case the glow was inhibited below a certain temperature, and above this it became increasingly difficult to blow it away.

If Lord Rayleigh's assumption be adopted, it follows from these results that the typical poisons studied act by reducing the rate of propagation of the glow in the gas mixture. Complete inhibition of the luminous oxidation marks the limit of this effect with increasing concentration of inhibitor. It is very probable, therefore, that oxygen acts in the same way as the more active poisons. A discussion of the possible mechanism of inhibition is given later. These considerations might seem inapplicable to the conditions under which the glow of phosphorus is generally seen, *viz.*, as a surface luminosity. The establishment of this intense surface oxidation is, however, often preceded by the passage of a luminous pulse through the gas mixture, resulting in the production of ozone, which tends to localise the reaction.

#### *The Influence of Temperature on the Action of Inhibiting Substances.*

The effect of "poisons" depends both on the pressure and on the temperature. The influence of pressure was investigated by Centnerszwer (*Z. physikal. Chem.*, 1898, 26, 1). Phosphorus was introduced into a mixture of oxygen with the inhibiting vapour, and the pressure was reduced until the glow appeared. In every case the limit was lower the greater the concentration of the inhibitor. The present experiments represent an attempt to make a similar systematic study of the influence of temperature. Ethylene has been used, since it is not only a strong poison, but is inert towards phosphorus. Probably it is typical, however, for experiments made with carbon disulphide and ethyl iodide gave similar although less consistent results.

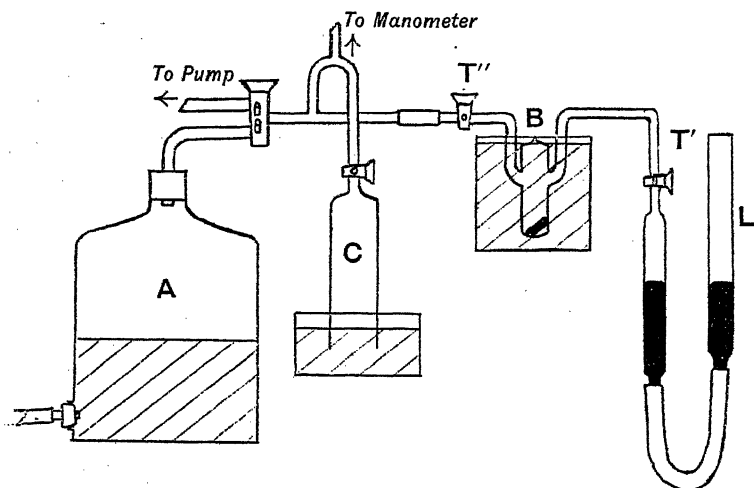
The apparatus used is shown in Fig. 3. Ethylene was prepared from phosphoric acid and absolute alcohol, washed by water and sulphuric acid, and collected over water in A. Between 2—5 g. of purified phosphorus were sealed up in the tube B of 30 c.c. capacity, which was immersed in a freezing mixture and evacuated, with the tap T' closed and the space below it filled with mercury. B was then put in melting ice, and ethylene was admitted from A. After allowing time for diffusion, moist air or oxygen was passed in from C until the total pressure was that of the atmosphere. The tap T'' was then closed and T' opened. B was heated gradually on a water-bath over a resistance mat, and the temperature at which the glow appeared was recorded. During heating, the pressure in the apparatus was kept constant by adjusting the levelling tube,



L. Between successive experiments with different ethylene-air mixtures, the space below T' was filled with mercury, T' was closed, B was cooled, and the apparatus was alternately evacuated and filled with air a number of times. Some consecutive pairs of observations were made with the same phosphorus, in which a definite partial pressure of ethylene was established first in air and then in oxygen. Such readings were strictly comparable, and differed by less than 3°. The oxygen-ethylene mixtures frequently detonated shortly after the phosphorus had begun to glow.

Experiments were made at constant volume by raising the tube L (Fig. 3). The resulting increase in pressure amounted at the

FIG. 3.



highest temperature employed to approximately half an atmosphere, and a corresponding increase in the glow temperature of 5–10° was recorded. The results are shown graphically in Fig. 4.

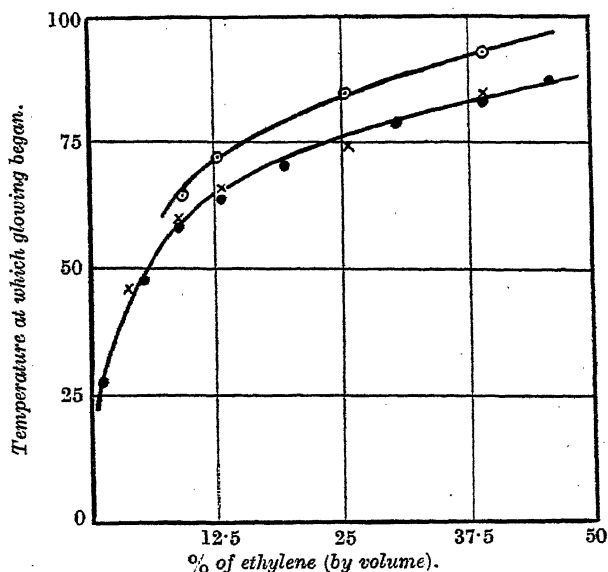
The main source of error in these experiments was in the observation of the glow. Even with thoroughly rested eyes it was difficult to determine in some cases whether a glow was occurring or not, especially with the high ethylene concentrations.

Two points of special interest are brought out by these results. The temperature at which the glow first occurred appeared to be determined by the concentration of the ethylene, irrespective of whether it was mixed with air or oxygen; also the luminous oxidation was inhibited at temperatures well above the normal ignition-point of phosphorus, which is about 60°.

Although these experiments leave little doubt as to the absence

of luminous oxidation below a definite temperature, a number of tests were made to determine if any non-luminous oxidation occurred. Purified phosphorus (1–2 g.) was sealed in tubes of 40 c.c. capacity (1.5 cm. diameter), having a quill tube fused to one end and drawn down to a capillary about 20 cm. from the wider tube. The whole tube up to the capillary was cooled in a freezing mixture and evacuated; the freezing mixture was replaced by melting ice, moist ethylene and air were admitted in the desired proportions, as indicated by the pressure, and the tube was sealed at the capillary. Two series of bulbs, containing 8% and 26%, respectively, of

FIG. 4.



○ Ethylene-air mixtures at constant volume. × Ethylene-oxygen mixtures at constant pressure. ● Ethylene-air mixtures at constant pressure.

ethylene were heated in the dark in a thermostat at 48° for 2 months, when they were opened by breaking the capillary under mercury, the bulb being inverted and cooled in ice. Any oxidation would be indicated by a rise of mercury in the stem, correction being made for change in barometric height. The bulbs containing 8% of ethylene exhibited a decrease in pressure of 2–12 cm. of mercury, whilst for those with 26% the decrease varied between 2–6 cm. Control tubes containing no phosphorus were unaltered. Further experiments are being made to verify that this slow rate of oxidation is maintained.

These results show that absorption of oxygen occurs when the

luminous oxidation is inhibited, which is analogous to Lord Rayleigh's observation of a slow non-luminous oxidation in moist oxygen at atmospheric pressure (*Proc. Roy. Soc.*, 1924, *A*, 106, 1).

### *Discussion.*

Any account of the mechanism of inhibition must explain why either an increase in temperature or a decrease in pressure tends to produce the glow. The former involves at least two factors, since both the vapour pressure of the phosphorus and the potential rate of reaction increase. The experiments described have shown that inhibition can extend to 90°, which is much above the normal ignition temperature of phosphorus. Moreover, the "glow temperature" does not depend on whether air or oxygen is used as a diluent for the ethylene. When the glow is prevented, the tendency for the reaction to occur is demonstrated by the slow non-luminous oxidation which was observed at 48°. At some stage, depending on the ethylene concentration, the impediment is overcome and a wave of luminosity passes through the mixture, the subsequent oxidation being accelerated by the formation of ozone. Again, on slowly decreasing the pressure in a mixture of ethylene and oxygen, the partial pressure of the phosphorus will remain constant in the presence of the solid. In effect, therefore, the proportion of combustible vapour in the mixture is being increased, which in itself would be expected to favour flame propagation.

Several analogous cases have been recorded. White found that the vapours of benzene, acetaldehyde, acetone, and ether had "a powerful inhibitory effect on the propagation of flame in carbon disulphide-air mixtures" (*J.*, 1922, 121, 2561). The addition of 0.025% of ether, for example, necessitated the use of 25% more carbon disulphide if the mixture was to propagate flame. In Dixon's experiments on the phosphorescent flame of carbon disulphide, a very much higher temperature was required to produce ignition when a small amount of ethylene was added (*Rec. trav. chim.*, 1925, 44, 305). Further examples are furnished by the many organic sulphur compounds studied by Delépine (*Bull. Soc. chim.*, 1922, 31, 762). These contain the group  $C=S$ , or  $P=S$ , and undergo a luminous oxidation at room temperatures, which is inhibited by ether, acetone, and pyridine. Here also a decrease of pressure or an increase of temperature will restart the luminescent reaction after it has been arrested.

The experiments described have shown that the addition to air of typical inhibitors renders it easier to blow the glow from a phosphorus surface, and that increase in temperature diminishes this action. An analogy is thus established between the action of

excess of oxygen and that of stronger poisons, in that both prevent the propagation of the glow in the gas. A tentative explanation of the mechanism was put forward by Lord Rayleigh, who suggested that in the propagation of the glow the products of the reaction in one layer acted as catalysts in the next. These catalytic particles are supposed to be rendered inactive by the adsorption of the inhibiting molecules, when the reaction stops. A similar view has been adopted by Dixon to explain the inhibition of the phosphorescent flame of carbon disulphide.

The author wishes to thank Professor H. B. Baker, F.R.S., for his kind interest and advice throughout this research. He is indebted to the Department of Scientific and Industrial Research for a maintenance grant, and to the Trustees of the Dixon Fund for a grant for the purchase of apparatus.

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### CLXXIII.—*An Improved Hydrogen Sulphide Generator.*

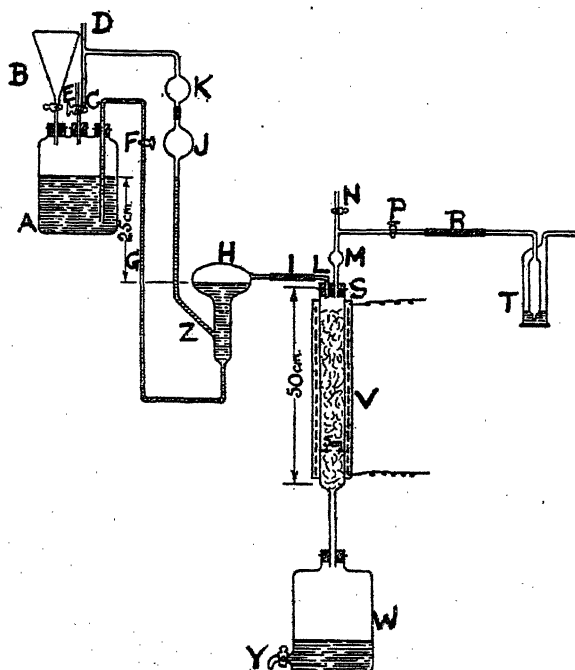
By HENRY GEORGE DENHAM and JOHN PACKER.

AN automatic hydrogen sulphide generator for laboratory installation has been described by Steele and Denham (J., 1920, **117**, 527). Since then the present authors have redesigned certain portions of the apparatus and the modified generator has given such highly satisfactory results during constant use for the last two years that a description of it is considered justified. A laboratory fitted with one of these generators would have a potential and practically unlimited supply of hydrogen sulphide always at hand at the negligible cost of the electric current needed to keep the generator heated.

The following is a description of the apparatus. A is the acid-holder of about 6 litres capacity; B a tap-funnel for use in filling A; C a two-way tap so that A can be connected either to the tube D which leads to an outside flue, or to E; F is a large-bore tap situated at a higher level than the acid in A; H is a reservoir of 600–700 c.c. capacity for retaining hydrogen sulphide generated, but not withdrawn from the apparatus; J is a bulb of about 150 c.c. capacity, situated a few cm. above the highest level of acid in A; K is a 100 c.c. bulb; L is a piece of capillary tubing of 2 mm. bore and of about 8 cm. total length, used to prevent a too rapid flow of acid into V, connected to the reservoir H by a piece of pressure

tubing I (wired on); M is a small 10 c.c. bulb, N and P are taps, R is thick-walled rubber tubing, inserted for flexibility so that the rubber stopper S can be easily removed; T is a wash-bottle containing water, through which the hydrogen sulphide is supplied to the distributing taps and mains; V is a tube of fused silica, the upper portion of which is about 50 cm. long and 5 cm. internal diameter whilst the lower part is of 2 cm. internal diameter, fitted by a tight rubber stopper into the reservoir, W, of 6 litres capacity, which receives the spent acid; Y is a tap through which the spent

FIG. 1.



acid is withdrawn, connected to a waste drain. The tube V is heated electrically to a temperature of approximately  $80^{\circ}$ . The winding (total resistance 100 ohms) is made over a thin piece of asbestos paper with nichrome wire of 1 ohm per foot resistance, and is well covered with many thicknesses of asbestos paper. In the authors' generator, this winding is connected through an ammeter and adjustable resistance to a storage battery in such a way that it can be connected either with the full battery of 110 volts or a portion of it giving 60 volts. A current of just over 1 amp. is sufficient to heat the tube V up to the working tem-

perature in from 10 to 15 minutes, whilst a current of 0.6 amp. will maintain this temperature.

*Mode of Operation.*—The tube V is packed with lumps of iron sulphide. The acid-holder is filled by means of the funnel B with commercial hydrochloric acid diluted with an equal volume of water, and the funnel tap turned off. The taps F and N are turned on and the tap C is turned so as to connect the acid-holder to E, through which air is blown until the siphon, G, fills. Tap N is then turned off and tap E turned so as to connect the acid-holder with the tube D. The reservoir H fills to the side-tube level with acid which then runs over into V and, provided the tube V has been sufficiently heated, hydrogen sulphide is generated as soon as a few drops run over, and drives the acid back into H, where the gas is stored until drawn off through the tap P and wash-bottle T. The acid is completely neutralised long before it has percolated through the heated column of sulphide. The side-tube Z and bulbs J and K are provided as an escape for hydrogen sulphide should an excessive amount be generated owing to some abnormal cause. This prevents hydrogen sulphide from getting into the siphon and putting the generator out of action. When the generator is not in operation and the tube V not heated, tap F is kept turned off.

*General Remarks.*—The capacity of this generator is practically the same as that of the one formerly described, whilst almost theoretical yields of hydrogen sulphide are always available at a steady and convenient pressure. It has the following advantages over the older form: (1) It is completely automatic in operation. From this point of view electrical heating is a great advantage over steam heating, whilst the use of silica instead of glass for the tube V overcomes the trouble formerly experienced of cracking, due to alternate heating and cooling. (2) There is no leakage of acid, as it never comes into contact with the rubber stoppers or connexions (except at I during a portion of the cycle of operations). (3) Provided the tube D is carried to a suitable flue, there is no smell of hydrogen sulphide.

The hydrogen sulphide is distributed throughout this building in composition (lead) gas-pipes of  $\frac{1}{4}$  in. internal diameter without any serious loss of pressure. After 3 years the attack on these pipes appears scarcely to have penetrated beyond the inner surface, although in the experience of one of the authors in the sub-tropical climate of Brisbane these pipes were seriously attacked, but this could probably be overcome by the use of drawn copper tube.

CLXXIV.—*The Doubtful Existence of Aurous Oxide.*

By WILLIAM BRANCH POLLARD.

It has been found that mercurous nitrate and chloroauric acid react to form gold and a basic auric compound (this vol., p. 529), and not "aurous oxide" as claimed by Figuier (*Ann. Chim. Phys.*, 1844, **11**, 339) and Krüss (*Annalen*, 1887, **237**, 276). In consequence of this, "aurous oxide," prepared in other ways, has been examined to see if it might not consist of colloidal gold and auric hydroxide. Analogous substances are known, such as Purple of Cassius, in which metallic hydroxides function as protective colloids.

From the equation  $3\text{Au}_2\text{O} = 4\text{Au} + \text{Au}_2\text{O}_3$  it is clear that the determination of gold and oxygen cannot show whether the substance is aurous oxide or a mixture of gold and auric oxide in these proportions. This possibility was overlooked by Krüss, whose analyses are therefore inconclusive. Krüss's claim is, moreover, unsupported by any chemical evidence showing that aurous compounds can be formed from "aurous oxide."

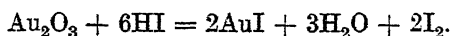
## EXPERIMENTAL.

In attempts to prepare "aurous oxide" from potassium bromoaurate by Krüss's method, if an excess of potassium bromide was present, only metallic gold resulted. "Aurous oxide" was decomposed when heated with solutions of potassium bromide, but was much less decomposed by solutions of sodium chloride. As potassium bromide is a by-product in the formation of "aurous oxide," it is surprising that Krüss was able to obtain his substance in the proportions required by theory.

By the following slight modification it was found possible to work at room temperature. Gold (1.0 g.) was converted into chloroauric acid, made up to 1 litre with saturated sodium chloride solution, and reduced to the aurous state with sulphurous acid. The solution, now colourless, was made slightly alkaline with caustic soda. Very little precipitation occurred at first, but a black, colloidal substance separated on standing. Heat caused the precipitation to occur rapidly. The formation of the substance is therefore quite unlike that of metallic hydroxides, but is highly suggestive of the decomposition of aurous compounds.

The substance formed a dark blue, colloidal suspension when washed with cold water, but could generally be washed with hot water. With hydrochloric or hydrobromic acid it instantly formed metallic gold and chloroauric or bromoauric acid; the reaction did not suggest the slow decomposition which takes place in aurous

compounds. The addition of alkali metal chlorides or bromides to the corresponding acids failed to produce aurous compounds (Lenher, *J. Amer. Chem. Soc.*, 1913, **35**, 547). Hydriodic acid gave gold, aurous iodide, and iodine; with excess of the reagent, aurous iodide passed into solution. This reaction resembles that of hydriodic acid and auric oxide:



Although these reactions were known to earlier workers, no reason has been given to explain why iodine should be liberated by "aurous oxide."

With a solution of sodium sulphite, the substance formed sodium aurosulphite and left a residue of gold which had the same black colour as the original substance. With sodium thiosulphate, it formed sodium aurothiosulphate and left a residue of black gold. In both these cases an aurous compound is formed, but only a third of the gold takes part in the reaction and this has to undergo reduction.

When the substance was heated with strong nitric acid a residue of gold was left and a yellow solution was formed which, on dilution, hydrolysed with the separation of auric hydroxide.

When heated with potassium bromoaurate solution, gold dissolved and was deposited, on cooling, in shining crystals according to the equation  $\text{AuBr}_3 + 2\text{Au} \rightleftharpoons 3\text{AuBr}$ .

When the substance was heated with potassium bromide solution, a residue of brown gold was left and gold passed into the solution, which then became strongly alkaline. Potassium iodide behaved in the same way, but was more energetic in its action. Sodium chloride solutions were much less reactive. Although no previous reference could be found, auric hydroxide was shown to behave in exactly the same way, dissolving even in strong sodium chloride solution which thus became alkaline. The reaction, however, was most marked in the case of potassium iodide.

The substance was scarcely attacked by dilute caustic soda, but with strong solutions sodium aurate and metallic gold were formed. Auric oxide was slowly attacked by weak but rapidly attacked by strong solutions of caustic soda. This explains why Krüss found it necessary to employ "very weak potash" in the formation of his "aurous oxide," strong alkali preventing its formation just as strong hydrochloric acid prevents the formation of Purple of Cassius.

Although numerous reactions have been tried, in no case has any definite aurous reaction been discovered, the substance always behaving as a mixture of gold and auric hydroxide. As the sub-



stance is highly colloidal, any attempts at a mechanical separation into gold and auric hydroxide would present very great difficulty. Experiments were made, however, to see whether auric hydroxide could act as a protective colloid in the manner suggested.

Auric hydroxide prepared by the magnesia process was washed in a centrifuge with cold water until it began to pass into colloidal suspension just as Krüss's "aurous oxide" does. Portions were then taken, made alkaline with caustic soda, and partly reduced to gold by dilute solutions of various reducing agents. Little reaction occurred at first, but when the solutions were warmed or made more alkaline reduction set in. Further additions of reducing agent were made until the action was judged to have proceeded far enough; the precipitates were then separated in a centrifuge and washed. Black precipitates which appeared to be identical with Krüss's "aurous oxide" were thus obtained, with hydrazine, phenylhydrazine and formaldehyde as reducing agents. With sodium peroxide as reducing agent, a brown precipitate was obtained which transmitted red light but was otherwise identical with "aurous oxide."

No evidence has therefore been obtained to show that aurous oxide exists; its chemical and physical properties are those of a mixture of gold and auric hydroxide.

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## CLXXV.—*Studies with the Microbalance. Part IV.* *The Photochemical Decomposition of Silver Iodide.*

By ERNST JOHANNES HARTUNG.

EXPERIMENTAL investigation of the action of light on silver iodide has hitherto furnished no definite result; when insolated in air, the substance slowly becomes greenish-grey, but the actual amount of chemical change appears to be very small and no free halogen has been detected. Koch and Schrader (*Z. Physik*, 1921, 6, 127) illuminated very minute particles of silver iodide, suspended between the charged plates of a condenser, but could find no changes in weight greater than 1—2%. Koch and Vogler (*Ann. Physik*, 1925, 77, 495) examined the space lattice of silver iodide by X-ray methods; after exposure to sunlight for 4 months, no free silver could be detected, although this was readily found on illumination of silver chloride and bromide for much shorter periods. Various other methods have given negative or indefinite results, although the consensus of opinion appears to be that the change is different

in nature from the decomposition of the bromide and chloride. Some years ago, the author showed (J., 1922, 121, 689) that very thin films of silver iodide deposited on vitreous silica lost weight appreciably when exposed in air to sunlight; the losses were very much smaller than those found for the bromide and chloride, but there was no doubt as to their reality. A thorough study of the question has now been made by means of the Steele-Grant microbalance, on the general lines used successfully in the cases of the bromide and chloride (J., 1924, 125, 2198; 1925, 127, 2691) and it has been found that the photochemical decomposition of silver iodide is analogous to that of the other halides of silver; iodine is liberated and, under suitable conditions, the action may be made almost complete. The microbalance employed carried a load of 105 mg. and weighed with precision to  $10^{-4}$  mg.; it had been thoroughly tested for 2 years and was used in very favourable circumstances. The general plan of the work was to iodinate thin films of chemically deposited silver until pure iodide had been formed. The films were then exposed to sunlight for various periods in oxygen, hydrogen, or nitrogen in the presence of a suitable iodine absorbent and subsequently reweighed. The insolated material was then treated in various ways in attempts to discover its nature. A series of experiments on the rate of iodination of silver, and of previously insolated silver iodide, was also made.

*Preparation of Films of Pure Silver Iodide.*—Light vitreous silica sheets were silvered in the well-known tartrate solution and ignited at  $400^{\circ}$  in a small electric furnace to drive off all occluded matter. After weighing, these films were hung over carefully purified iodine at room temperature; pearly-yellow iridescent silver iodide was rapidly formed and the films were then reweighed. Comparison of the weights with those calculated from the weight of silver taken showed an average discrepancy of 1 part in 1300 parts; the average weight was 0.34 mg. and the thickness about 0.0002 mm. Precipitated silver iodide is known to adsorb iodine readily, but no evidence of adsorption, or of the formation of polyiodides, was obtained in these experiments.

*Photochemical Decomposition of Silver Iodide.*—The glass apparatus in which the films were sealed, prior to insolation, was similar to that employed for silver bromide and has already been described (*loc. cit.*). Great care was necessary to prevent damage to the films by flame gases during sealing operations, but repeated tests showed that a good counter-current of purified air gave adequate protection. Before exhaustion, the vessel was filled with oxygen, hydrogen, or nitrogen, which had been specially purified and filtered. Experiments showed that at atmospheric pressure decomposition

of the silver iodide was very slow, even after prolonged exposure to strong sunlight, but was hastened by diminution of pressure. The apparatus was therefore exhausted either to 10 mm. pressure or as completely as possible. As heating of the glass walls was inadmissible owing to the sensitive nature of the films, adsorbed gas must have been released slowly during insolation; this is denoted by "res." (*i.e.*, "residual") in Table I, to indicate that the pressure in the apparatus was less than 0.001 mm. at the time of sealing off from the pump. As absorbent for the liberated iodine, a roll of clean copper gauze was employed at first; this metal is particularly efficient in removing chlorine and bromine from a gas phase, but it was not successful with iodine. Inspection of the gauze after prolonged irradiation of the iodide film showed only slight evidence of tarnish, and at the same time the decomposition of the silver iodide had been very slow. Thus, after more than 6 months' exposure on the roof of the laboratory in an exhausted vessel containing copper gauze, a film of silver iodide weighing about 0.4 mg. had lost only 16.6% of its total iodine. This tardiness of decomposition indicated that the partial pressure of iodine vapour above strongly illuminated silver iodide is very small, for copper tarnishes readily above solid iodine at room temperature (partial pressure of vapour 0.2 mm.). It was subsequently found that silver absorbs iodine vapour with extreme readiness, even when the partial pressure of the halogen is very small, and consequently the lower portion and side-tube of the apparatus were silvered internally before introduction of the photosensitive film. During insolation, this silver deposit was shielded from radiation by opaque wrappings and a marked increase in the rate of decomposition of the halide was observed at once. In all subsequent experiments, therefore, silvering was adopted in order to render the absorption of iodine as complete as possible. The amount of radiant energy absorbed during insolation could not be measured, owing to the progressive change in the colour, opacity, and reflecting power of the films, but a fair indication is given in each case by the length of exposure in days. After a definite period of insolation, during which the film became deep slate-grey, the apparatus was opened under exhaust and purified nitrogen gradually admitted. The film was then removed and weighed; subsequent treatment consisted usually of re-iodination, but attempts were also made to analyse the product of insolation. Table I summarises the results of the experiments, weights being given in mg., and the columns headed  $F_1$  and  $F_2$  denoting the weights of the films after exposure and after re-iodination, respectively. It is evident that decomposition of the silver iodide proceeded very extensively, but only when the apparatus was exhausted;

TABLE I.

TABLE I.

Expt.	AgI.		F <sub>1</sub> .	F <sub>2</sub> .	% I lost.	Days.	Gas in apparatus.
	Ignited Ag.	Found. Calc.					
1	0.1137	0.2475	0.2476	0.1250	0.2564	91.6	84 H <sub>2</sub> res.
2	0.1814	0.3954	0.3948	0.2102	0.3966	86.5	42 " "
3	0.1120	0.2439	0.2438	0.1300	0.2452	86.3	52 N <sub>2</sub> "
4	0.1175	0.2558	0.2557	0.1335	0.2571	88.4	44 " "
5	0.0701	0.1521	0.1526	0.0795	0.1552	88.5	36 " "
6	0.2622	0.5705	0.5707	0.3355	0.5721	76.2	83 Air "
7	0.1095	0.2386	0.2383	0.1172	0.2402	94.0	89 O <sub>2</sub> "
8	0.1884	0.4101	0.4100	0.2548	0.4116	70.0	81 " "
9	0.1884	0.4095	0.4100	0.4040	0.4153	2.5	86 O <sub>2</sub> 10 mm.
10	0.1561	0.3396	0.3398	0.3341	0.3439	3.0	80 " "
11	0.1797	0.3907	0.3911	0.3686	0.3905	10.5	90 N <sub>2</sub> "
12	0.1775	0.3863	0.3863	0.3775	0.3869	4.3	40 " "

at 10 mm. pressure, the change was hindered in a remarkable manner. The nature of the residual gas in the apparatus seems to exert little influence and, in particular, the claim that oxygen is necessary is seen to be unfounded. Moreover, the extent of decomposition depends less on the period of exposure than on the thickness of the film, this being approximately proportional to the weight in each case. When all the factors are favourable, as in Expt. 7, decomposition is nearly complete. Certain minor irregularities in the results find a ready explanation in small variations in shape of the apparatus, which affect the ease of diffusion of the liberated iodine to the absorbing silver surface. There can be no doubt, however, that the products of insolation of silver iodide are silver and iodine, and the reason why extensive change is found only in very thin films is because of the opacity of the liberated silver and its very powerful attraction for iodine vapour. There is no evidence of the formation of any sub-iodide.

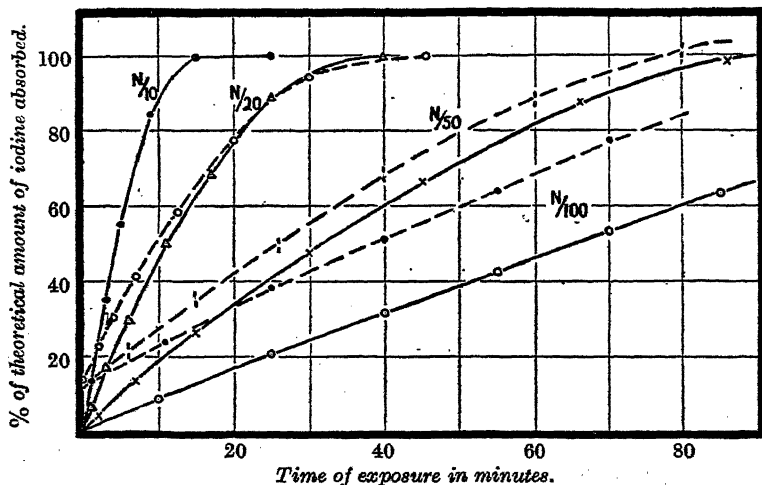
On re-iodinating the product of insolation, rapid restoration of the former yellow colour of the film took place and the weight was then usually rather greater than that of the original silver iodide. This behaviour was found with the chloride and bromide also and is believed to be due to slight oxidation of the insolated film during manipulation; the discrepancies are usually slight and, except for Expt. 1, are largest when oxygen in appreciable amount has been present in the exposing vessel (Expts. 9 and 10). Many attempts were made to analyse the product of insolation by methods which were devised for the filtration of very small amounts of material (this vol., p. 840), but no procedure for the accurate estimation of silver, or of silver iodide, in less than 0.5 mg. of a mixture of the two could be found. It was hoped to effect separation by suitable reagents, but solvents for silver (*e.g.*, nitric acid) removed the metal imperfectly from the iodide, whilst solvents for silver iodide (*e.g.*, silver nitrate, thiosulphates, cyanides) all attacked thin films

of silver rapidly in the presence of oxygen. Solution of both silver and silver iodide was easily effected by ammonium cyanide, which was then treated with acetic or hydrochloric acid; this precipitated all the iodide, and the remainder of the silver as either cyanide or chloride, but in each case the ammonium salt left in solution increased the solubility of the silver salts so markedly that no accurate results could be obtained. Also, estimation by simple evaporation of the ammonium cyanide solution to dryness was rendered useless by the formation of ammonium formate. Another attempted method consisted in evaporating the product of insolation with hydrochloric acid; the iodide was not affected by this treatment, but conversion of the silver presumably present into the chloride was so slow and imperfect that success was impossible. Finally, the attempts at analysis had to be abandoned, after showing that treatment of the product of insolation with silver iodide solvents left a residue of practically pure silver.

*Rate of Iodination of Silver Films.*—Further evidence as to the nature of the product of insolation of silver iodide was obtained by comparing its rates of re-iodination with those of pure silver. The apparatus and method have been described previously for the case of silver bromide (J., 1924, 125, 2204); the experiments were carried out in a thermostat at 25° (regulated to 0.1°) and at first solid iodine was placed in the iodinator, giving a partial pressure in the vapour phase of 0.3 mm. However, silver films were attacked so rapidly that conversion into iodide was complete in less than 2 minutes and accurate measurements were impossible. Solutions of iodine from  $N/10$  to  $N/100$  were therefore made in  $N$ -aqueous potassium iodide, and the partial pressures of the halogen above these solutions (not measured) were sufficiently small to give convenient rates of iodination. The results obtained are shown in Fig. 1, in which the iodine absorbed, as percentage of that necessary to form pure silver iodide, is plotted against the total time of iodination in minutes. The continuous curves indicate iodination of pure silver, and the broken curves iodination of the product of insolation of silver iodide, which contained an average of 14% of the total original iodine at the start. In each case, the total area of the film was 146 sq. mm. and the thickness about 0.00015 mm., so that the curves are fairly comparable. The rapid increase in the speed of addition of the halogen as the solution increases in concentration is shown, as well as the striking similarity in speed between silver and insolated silver iodide for the same concentration of iodine which is evident from the approximate parallelism of each pair of curves. This is strong presumptive evidence that one of the products of insolation is silver itself, although, of course, differ-

ences in the physical state of the liberated metal may be expected to alter the rates of iodination very considerably, and indeed do so in the cases of the chloride and bromide. The peculiar phenomenon of an optimum halogen concentration which was discovered in the case of chlorine (J., 1925, 127, 2696) has no parallel with iodine, where the rate of addition of the halogen steadily increases as the concentration in the gas phase rises. No evidence of the formation of sub-iodides or poly-iodides is indicated.

FIG. 1.



### Summary.

1. The photochemical decomposition of silver iodide has been studied by means of the microbalance.

2. The maximum percentage loss of total iodine in thin films of silver iodide when suitably insulated was: in hydrogen 91.6%, in nitrogen 88.5%, and in oxygen 94.0%.

3. Evidence is adduced to show that the photochemical decomposition products are silver and iodine, that oxygen is not necessary for the change, and that extensive action is found only with extremely thin films at low gas-pressure in the presence of silver as iodine absorbent.

4. The rates of iodination of silver and of previously insulated silver iodide have been studied; close agreement exists between them for similar concentrations of iodine vapour.

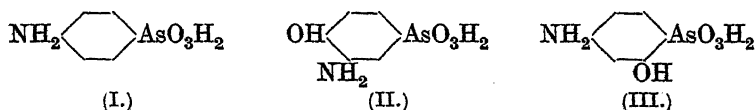
5. No evidence of the formation of silver sub- or poly-iodides has been found.

# CLXXVI.—*Trypanocidal Action and Chemical Constitution. Part V. Arylsulphonamides of some Phenylarsinic Acids.*

By LESLIE FRANK HEWITT, HAROLD KING, and WILLIAM OWEN MURCH.

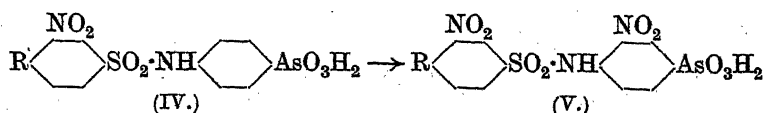
PARTS I to IV in this series were almost solely devoted to the preparation, properties, and trypanocidal activity of arylamides of phenylarsinic acids, the common feature of the compounds described being the amide link,  $-\text{CO}\cdot\text{NH}-$ . The present communication is designed to fill the gap in our knowledge of some of the corresponding sulphonamides, with the common link,  $-\text{SO}_2\cdot\text{NH}-$ , a group of which only two representatives, both non-amphoteric, have hitherto been described.

*m*-Nitrobenzenesulphonyl and *m*-nitro-*p*-toluenesulphonyl radicals have now been introduced into the amino-group of 4-aminophenylarsinic acid (I), and the former radical into the amino-groups of 3-amino-4-hydroxyphenylarsinic acid (II) and 4-amino-2-hydroxyphenylarsinic acid (III).



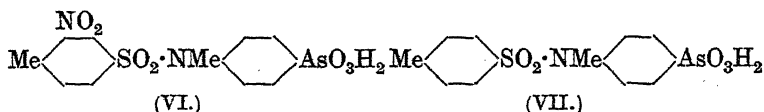
For this purpose, the most convenient and by far the most effective method is a modification of the Schotten-Baumann method devised by Fischer and Bergell (*Ber.*, 1902, 35, 3779) for the preparation of the  $\beta$ -naphthalenesulphonyl derivatives of amino-acids. The reaction with 3-amino-4-hydroxyphenylarsinic acid (II), an acid which is sensitive to caustic alkali, necessitates the use of sodium carbonate, and under these conditions a complex mixture results containing in all probability *O*-sulphonic esters and disulphonamides.

3'-Nitrobenzenesulphonyl- (IV; R = H) and 3'-nitro-4'-toluenesulphonyl-4-aminophenylarsinic acid (IV; R = Me) on further nitration yield exclusively one dinitro-acid (V), the constitution following from the products of hydrolysis.



3'-Nitro-4'-toluenesulphonyl-4-methylaminophenylarsinic acid (VI), which is the methylation product of (IV; R = Me), was obtained by

the action of methyl sulphate and alkali at 100°. It was unobtainable by methylation at room temperature, although 4'-toluenesulphonyl-4-methylaminophenylarsinic acid (VII) was readily formed under these conditions. The latter acid on solution in sulphuric acid at room temperature was completely hydrolysed and gave an



80% yield of 4-methylaminophenylarsinic acid, an acid which is not new. This is, however, the best method for its preparation.

The seven nitro- and dinitro-arsinic acids aforementioned on reduction with ferrous chloride and alkali gave the corresponding amino-compounds quite smoothly and in good yield. When tested for trypanocidal activity on mice infected with *Trypanosoma equiperdum*, they were found to be without exception completely inactive on any dose, including the maximum tolerated, although in structure they differ from the active amides of previous communications only in the replacement of  $-\text{CO}\cdot\text{NH}-$  by  $-\text{SO}_2\cdot\text{NH}-$ . This is a surprising result. It might be ascribed to the presence of the strongly acidic hydrogen atom of the  $-\text{SO}_2\cdot\text{NH}-$  group in comparison with that contained in the  $-\text{CO}\cdot\text{NH}-$  group, but this was negated by the inactivity of 3'-amino-4'-toluenesulphonyl-4-methylaminophenylarsinic acid derived from (VI) by reduction. It is, however, possible to proceed a step further in the analysis of this anomaly.

Ehrlich first advanced the theory that the real active trypanocidal agent in arsenicals is the tervalent arsenic stage, basing it on the two groups of observations, that cures of small animals artificially infected with trypanosomes could be effected by primary quinquevalent arsenic acids and by the corresponding tervalent arseno-compounds and arsenious oxides, but *in vitro*, i.e., outside the animal body, arsenic acids and arseno-compounds had negligible action on trypanosomes, whereas the oxides were very highly active. The view of the importance of the tervalent arsenious oxide has received further support from the experiments of Voegtlin and his associates in Washington, who show that animal tissues are able to reduce the arsenic acids and oxidise the arseno-compounds to the arsenious oxide stage :

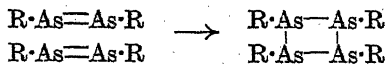


It was therefore of importance to test whether the oxides corresponding to the above-described inactive acids containing the sulphonamide group were trypanocidally active. 3'-Amino-4'-



*toluenesulphonyl-* and 3:3'-diamino-4'-*toluenesulphonyl-4-amino-phenylarsenious oxides* were prepared by reduction of the corresponding acids with sulphur dioxide and hydriodic acid, and the former oxide was examined in detail. It had a maximum tolerated dose of 0.01 mg. per g. of mouse, was thus twenty times as toxic as its parent acid and was completely devoid of trypanocidal activity on the infected animal, but at a dilution of 1 in 10,000 *in vitro* and 30 minutes' exposure, it rendered trypanosomes non-infective to the normal animal. As it can be calculated that this is just one-half the concentration which should obtain in the blood-stream of infected mice when injected intravenously with the maximum tolerated dose, it seems clear that the injected oxide must be de-activated by some body mechanism. Whatever be the ultimate chemical processes involved in the tissues which determine the distribution and fate of these acids or oxides before final excretion, it seems also certain that the sulphonamide linking must confer a general character on these molecules, independent of its orientation with respect to the arsinic acid group, which prevents the oxides from ever attaining a concentration inimical to the continued reproduction of the trypanosomes. Since the toxiphoric grouping is undoubtedly the group containing arsenic, the presence of the  $-\text{SO}_2\cdot\text{NH}-$  group is reflected in an altered distribution of affinities around the arsenic atom. Some light might be thrown on this by precision measurements of the relative reduction potentials of arsinic acids containing the amide link and their analogues with the sulphonamide link.

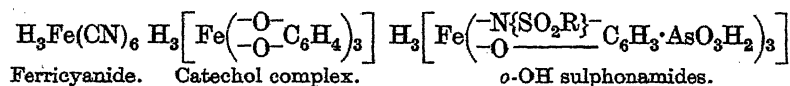
The *arseno-compounds* of 3'-aminobenzenesulphonyl-4-amino-phenylarsinic acid and 3'-amino-4'-toluenesulphonyl-4-aminophenylarsinic acid are white, whereas the arseno-compounds of their benzamide analogues are orange and almost all previously recorded arseno-compounds are yellow or orange. The colour of arseno-compounds is usually ascribed to the presence of the chromophoric grouping  $-\text{As}=\text{As}-$  analogous to the azo-chromophore,  $-\text{N}=\text{N}-$ . The view might therefore be advanced that the loss of colour in the white arsenobenzenes is due to formation of a bimolecular complex.



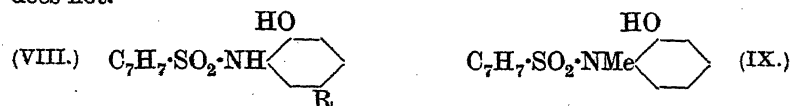
Michaelis and Schäfer (*Ber.*, 1913, 46, 1742) had found that the molecular weight of crystalline arsenobenzene and arsenotoluene in phenol as cryoscopic solvent agreed with the simple molecular weight. In the present instances, however, the experimental difficulties due to the peculiar properties of the substances have proved insurmountable.

In connexion with some of the compounds described in this communication, the observation has been made that compounds containing a hydroxyl group ortho to a sulphonamide group give a striking series of colour reactions with iron, nickel, cobalt, and copper salts in sodium hydrogen carbonate solution, which are destroyed by excess of caustic alkali or free mineral acid. The cobalt solutions show an absorption band in the yellow-green parts of the spectrum. If a purple alkaline solution of the iron complex of 3'-aminobenzenesulphonyl-3-amino-4-hydroxyphenylarsinic acid, for instance, be made neutral or weakly acid to litmus, a grey-black precipitate is formed, free from the anion of the precipitating acid, but with an iron-sulphur atomic ratio of approximately 1 : 1 and re-soluble in sodium hydrogen carbonate solution at least in part, with production of the original purple colour. The most reasonable view of the nature of the constituents of the coloured alkaline solutions is that a series of complex anions is formed analogous to the catechol complexes described by Weinland and Binder (*Ber.*, 1912, 45, 148) and based, at least in the case of iron, on the ferricyanide or ferrioxalate model; but whereas the iron-catechol complexes are of a stability to alkali comparable with that of potassium ferricyanide, the iron-*o*-hydroxysulphonamide complexes seem to be of a stability probably inferior to that of the ferrioxalates.

On this view, the acidic hydrogen atoms of the  $\text{-SO}_2\text{NH-}$  and  $\text{-OH}$  groups enter into the co-ordination complex.

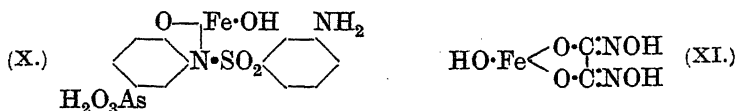


In support of this it is found that the benzamide analogues described in Part IV do not give these colour reactions, that *N-p*-toluenesulphonyl-*o*-aminophenol (VIII;  $\text{R} = \text{H}$ ) and *toluenesulphonyl-3-amino-4-hydroxybenzoic acid* (VIII;  $\text{R} = \text{CO}_2\text{H}$ ) give the colour reactions, but that *N-p-toluenesulphonyl-o-methylaminophenol* (IX) does not.



Incidentally Reverdin's so-called *O*-toluenesulphonyl-*N-p*-methylaminophenol (*Ber.*, 1909, 42, 1523) has been shown to be *N*-toluenesulphonyl-*N-p*-methylaminophenol. The greyish-black precipitate previously mentioned as being obtained on acidification of the purple iron solutions possibly has the constitution (X) analogous to the ferric oxalohydroxamate (XI) of Hantzsch and Desch (*Annalen*,

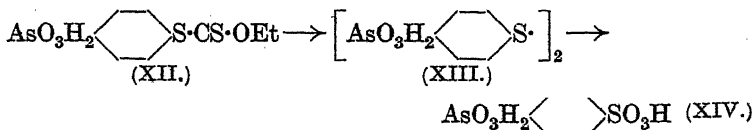
1902, 323, 24), but development of the purple colour by solution of (X) in alkali cannot be mere formation of a soluble salt of the arsenic



acid grouping, because the same colour is obtained from (VIII; R = H), where the salt-forming group is absent.

4-Amino-2-hydroxyphenylarsinic acid (III), its 3'-nitrobenzenesulphonyl- and 3'-aminobenzenesulphonyl-derivatives also give colour reactions with ferric and cupric salts in sodium hydrogen carbonate solution. It is possible that in these cases also co-ordination compounds, involving the arsinic acid and adjacent hydroxyl groups, are formed.

In this communication it is convenient to incorporate some observations on one of the simplest aromatic arsinic acids containing the sulpho-group, namely, *p*-sulphophenylarsinic acid. In 1919, one of the authors (K.) made an unsuccessful attempt to prepare the thiol analogue of salvarsan, and the experiments which follow arose out of that attempt. *p*-Aminophenylarsinic acid was converted into *p*-xanthylphenylarsinic acid (XII) by Leuckardt's method (*J. pr. Chem.*, 1890, **41**, 179) and this on oxidation on the boiling water-bath with 3*N*-nitric acid gave a mixture of the sparingly soluble diphenyl disulphide *pp'*-diarsinic acid (XIII) and the extremely soluble *p*-sulphophenylarsinic acid (XIV).



The latter acid is, however, more readily obtained by oxidation of the disulphide by boiling 6*N*-nitric acid. The disulphide and the sulpho-acid proved to be devoid of trypanocidal action. The sulpho-acid was converted into the corresponding *arseno-acid* by reduction with hypophosphorous acid, but owing to its very ready solubility in water this could not be isolated sufficiently pure for physiological testing. Dr. Voegtlin has also prepared this sulpho-acid and its arseno-derivative (*Physiological Reviews*, 1925, **5**, 91), but he informed us verbally that his method for the preparation was different from ours.

We are indebted to Miss F. M. Durham and Miss J. Marchal of this department for the painstaking care with which they have determined the toxicities and trypanocidal action of the compounds described in this paper.

## EXPERIMENTAL.

*4'-Toluenesulphonyl-4-aminophenylarsinic Acid.*—This acid, briefly described by Little, Cahen, and Morgan (J., 1909, 95, 1482) as being obtained by the Schotten-Baumann reaction, may be obtained in 74% yield by the Fischer-Bergell method of arylsulphonylation. Sodium *p*-aminophenylarsinate pentahydrate (1 mol.) dissolved in 5 parts of water was shaken with finely-powdered *p*-toluenesulphonyl chloride (2 mols.) and a few drops of ether for 30 minutes. *N*-Sodium hydroxide (1 mol.) was then added, and the mixture again shaken for 30 minutes. This sequence was repeated until 3 molecular proportions of *N*-alkali had been added. The arsinic acid obtained on acidification was sparingly soluble in boiling water, crystallising in microscopic rectangular plates, but readily soluble in boiling 90% formic acid, crystallising therefrom in needles and diamond-shaped plates.

*4'-Toluenesulphonyl-4-methylaminophenylarsinic Acid (VII).*—*4'*-Toluenesulphonyl-4-aminophenylarsinic acid (1 mol.) was dissolved in 2*N*-sodium hydroxide (2 mols.) and heated in the boiling water-bath with vigorous stirring while methyl sulphate (16 mols.) and an equivalent quantity of 2*N*-sodium hydroxide were run in simultaneously, the reaction of the fluid being faintly alkaline throughout. On acidification a 90% yield of the methylated acid was obtained. It is readily soluble in boiling water and crystallises in needles which are unstable and pass readily into large, hexagonal plates. From alcohol it crystallises in needles and from 90% formic acid, in which it is extremely readily soluble, in microscopic, rectangular plates (Found: S, 8.0.  $C_{14}H_{16}O_5NSAs$  requires S, 8.3%). This acid can also be obtained by methylation at room temperature.

*4-Methylaminophenylarsinic Acid.*—*p'*-Toluenesulphonyl-4-methylaminophenylarsinic acid was dissolved in  $3\frac{1}{2}$  volumes of concentrated sulphuric acid at room temperature, kept for 30 minutes, and then poured on to ice. The mixture having been made neutral to Congo paper, an 80% yield of *N*-methylaminophenylarsinic acid was obtained (Found: As, 32.6. Calc.: As, 32.4%). It is very soluble in *N*-hydrochloric acid and with nitrite gives an instant precipitate of fine needles of the nitroso-compound. On slight dilution, these rapidly transform into six-sided plates which give the Liebermann nitroso-reaction. This acid had a tolerated dose of 0.05 mg. per g. of mouse, and on this dose mice infected with *T. equiperdum* relapsed in the most favourable cases within 7 days.

*Sodium 3-Nitro-4-toluenesulphonate.*—The following process is an improvement on that of Otto and Gruber (*Annalen*, 1868, 145, 23)

and of Fichter and Bernoulli (*Ber.*, 1909, 42, 4309). *p*-Toluenesulphonic acid (100 g.) was heated with 380 c.c. of nitric acid (*d* 1.42) in the boiling water-bath for 30 minutes. The solution was poured into a litre of water and rapidly evaporated to dryness under reduced pressure. The residue, which crystallised in envelope-shaped plates, was re-evaporated with small quantities of water to remove all nitric acid, and the solution then neutralised with sodium carbonate. On concentration, a 72% yield of the *monohydrated sodium* salt was obtained (Found: Loss at 100°, 7.3.  $C_7H_6O_5NSNa \cdot H_2O$  requires  $H_2O$ , 7.0%. Found on dried salt: Na, 9.9.  $C_7H_6O_5NSNa$  requires Na, 9.6%). The *barium* salt, which is less soluble than the sodium salt and crystallises in creamy, glistening leaflets, was prepared by addition of barium chloride to a solution of the sodium salt (Found: Loss at 100°, 6.2.  $C_{14}H_{12}O_{10}N_2S_2Ba \cdot 2H_2O$  requires  $H_2O$ , 6.0%. Found on dried salt: Ba, 24.3.  $C_{14}H_{12}O_{10}N_2S_2Ba$  requires Ba, 24.1%).

In another experiment using 15 g. of acid and 50 c.c. of nitric acid, the solution obtained on pouring the product into water was extracted thrice with ether. The ethereal extract was freed from acids by extraction with alkali and on evaporation gave 0.75 g., a 6.3% yield, of *p*-nitrotoluene. The main bulk melted at 54°, as did a mixture with pure *p*-nitrotoluene, but a trace melted 10° higher, suggesting the presence of 2:4-dinitrotoluene.

**3'-Nitro-4'-toluenesulphonyl-4-aminophenylarsinic Acid** (IV; R = Me).—Sodium *p*-aminophenylarsinate was submitted to the action of *m*-nitro-*p*-toluenesulphonyl chloride (2 mols.) by the Fischer-Bergell process described above. The yield of required acid was 77%. It is sparingly soluble in boiling water and crystallises therefrom in minute, rectangular plates (Found: S, 7.8.  $C_{13}H_{13}O_7N_2AsS$  requires S, 7.7%). The maximum tolerated dose for mice is 0.3 mg. per g. of mouse and subsequent toxicities are expressed on the same basis.

**3'-Nitro-4'-toluenesulphonyl-4-methylaminophenylarsinic Acid** (VI).—This acid was obtained in 93% yield by methylation of the preceding acid by the process described for its analogue without the nitro-group. It is not formed in recognisable quantity by methylation at room temperature, using a large excess of methyl sulphate and a variety of concentrations of potassium or sodium hydroxide. It is soluble in 200 parts of boiling water and crystallises in feathery needles, but from alcohol in large, hexagonal plates and from 90% formic acid in diamond-shaped plates (Found: S, 7.3.  $C_{14}H_{15}O_7N_2SAs$  requires S, 7.4%). The maximum tolerated dose is 0.03 mg.

**3'-Amino-4'-toluenesulphonyl-4-aminophenylarsinic Acid**.—The nitro-acid (8.3 g.) was reduced with ferrous chloride and alkali as

described in previous papers of this series. The alkaline extracts (0.2*N*-NaOH) of the ferric hydroxide precipitate were neutralised to Congo-paper, and the crystalline amino-acid which separated was kept over-night. It was collected, dissolved in 140 c.c. of *N*-hydrochloric acid at 50°, and when precipitated by careful addition of saturated sodium acetate separated in small, prismatic needles. The first precipitation mother-liquors treated at 100° with ammonia and magnesium chloride gave a small quantity of *magnesium* salt which gave a further small proportion of the required amino-acid. The total yield was 73% (Found: S, 8.3.  $C_{13}H_{15}O_5N_2SAs$  requires S, 8.3%). This *amino-acid* is readily soluble in 2*N*- or 3*N*-mineral acids, the *hydrochloride* being precipitated in small, oblique rhombs by concentrated hydrochloric acid. The maximum tolerated dose is 0.2 mg.

*3'-Amino-4'-toluenesulphonyl-4-aminophenylarsenious Oxide*.—The foregoing acid (1.8 g.) was dissolved in 10.8 c.c. of water with the aid of 8.2 c.c. of concentrated hydrochloric acid. On addition of 0.45 g. of potassium iodide in a few drops of water there was rapid separation of iodine and a brown gum, but on passing sulphur dioxide for successive  $\frac{1}{2}$ -hour intervals with intermediate kneading of the now pale yellow gum, it eventually crystallised completely in almost quantitative yield. It was titrated by Ehrlich and Berthelm's method for *p*-aminophenylarsenious oxide (*Ber.*, 1910, 43, 917) (Found: 0.2185 g., dry, required 9.02 c.c. of *N*/10-iodine. Calc. for  $C_{13}H_{13}O_3N_2SAs$ : 9.06 c.c.). The agreement is fortuitous, as the product contained hydrochloride. It was dissolved in water, and the free *oxide* precipitated as a white, amorphous powder by addition of sodium hydrogen carbonate (Found: 0.2132 g. equiv. to 11.53 c.c. of *N*/10-iodine. Calc.: 12.04 c.c. Whence the purity was 96%). This arsenious oxide reduces ammoniacal silver solution only on warming. It is readily soluble in *N*-hydrochloric acid and diazotises and couples in the usual way. It is also readily soluble in 0.5*N*-sodium carbonate and 2*N*-ammonia but not in sodium hydrogen carbonate.

*3'-Aminotoluenesulphonyl-4-aminoarsenobenzene*.—The foregoing arsenious oxide (1.25 g.) was dissolved in water (6 c.c.) with addition of 6 c.c. of hypophosphorous acid (*d* 1.137) and a crystal of potassium iodide. The solution was stirred and the temperature slowly raised to 80°. The arsenobenzene separated in microscopic needles which were centrifuged off, washed first with water and then with sodium hydrogen carbonate solution, and finally with several changes of water. The crystalline character was retained throughout. The yield was 1.1 g. The same compound was also obtained in the crystalline state very readily by reduction of the corresponding acid

at 50—55° (Found : 0.1158 g. required 13.9 c.c. of *N*/10-iodine in the presence of sodium acetate. Calc. : 13.7 c.c. Found : As, as  $\text{Mg}_2\text{As}_2\text{O}_7$ , 22.6.  $\text{C}_{26}\text{H}_{26}\text{O}_4\text{N}_4\text{As}_2\text{S}_2$  requires As, 22.3%). This arseno-compound is white or of a pale cream colour. It is readily soluble in molten phenol, but insoluble in acetic acid. It is insoluble in mineral acids, but dissolves on addition of nitrite and then couples in the usual way. It dissolves in an equivalent amount of sodium hydroxide, but is precipitated as the sodium salt by a slight excess. It is also slowly soluble in sodium carbonate solution. The dried powder is very easily electrified and consequently very difficult to handle. The maximum tolerated dose is 0.1 mg.

*3'-Amino-4'-toluenesulphonyl-4-methylaminophenylarsinic Acid.*—This acid was obtained in 75.3% yield by reduction of the corresponding nitro-acid with ferrous chloride and alkali. It was purified by solution in *N*-hydrochloric acid and precipitation by sodium acetate (Found : S, 8.1.  $\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_2\text{SAs}$  requires S, 8.0%). This acid crystallises readily from boiling water in clusters of thin plates. It is readily soluble in warm *N*-hydrochloric acid, the *hydrochloride* crystallising in prisms. The *sulphate* and *nitrate* are sparingly soluble in their respective *N*-acids and both crystallise in fine needles. The maximum tolerated dose is 0.03 mg.

*3 : 3'-Dinitro-4'-toluenesulphonyl-4-aminophenylarsinic Acid* (V; R = Me).—This acid was prepared in 73% yield from 8.3 g. of 3'-nitrotoluenesulphonyl-4-aminophenylarsinic acid, dissolved in 25 c.c. of sulphuric acid and nitrated with 2 g. of nitric acid (*d* 1.42) in 2 g. of sulphuric acid. It crystallises from boiling water, in which it is sparingly soluble, in very small needles, and from glacial acetic acid, in which it is moderately soluble, in bunches of small, prismatic needles (Found : S, 6.9.  $\text{C}_{13}\text{H}_{12}\text{O}_9\text{N}_3\text{SAs}$  requires S, 6.9%). The maximum tolerated dose is 0.1 mg.

*3 : 3'-Diamino-4'-toluenesulphonyl-4-aminophenylarsinic Acid.*—This acid was prepared by reduction of the preceding dinitro-acid (9.2 g.) with ferrous chloride and alkali. The alkaline extracts of the ferric hydroxide gave 2.7 g. of acid by direct precipitation and 2.0 g. by way of the *magnesium* salt in hot ammoniacal solution. The total yield was 60%. This *diamino-acid*, precipitated from acid solution by sodium acetate, separates in small, rhomb-shaped plates. It is very soluble in dilute mineral acids and diazotises and couples with alkaline  $\beta$ -naphthol with a blood-red colour (Found : As, 18.9.  $\text{C}_{13}\text{H}_{16}\text{O}_5\text{N}_3\text{SAs}$  requires As, 18.7%). The maximum tolerated dose is 0.5 mg.

*3 : 3'-Diamino-4'-toluenesulphonyl-4-aminophenylarsenious Oxide.*—One g. of the preceding acid was dissolved in 4.5 c.c. of con-

centrated hydrochloric acid and 6 c.c. of water. Potassium iodide (0.25 g.) was added and sulphur dioxide passed for an hour. A crystalline salt separated in long, yellow needles (Found for anhydrous material: 0.1138 g. equiv. to 3.57 c.c. of *N*/10-iodine. Calc. for the pure dihydriodide: 3.97 c.c.). The remainder was dissolved in water, and the oxide precipitated with sodium hydrogen carbonate. The yield was 0.4 g. (Found for anhydrous oxide: 0.1623 g. equiv. to 8.41 c.c. of *N*/10-iodine.  $C_{13}H_{14}O_3N_3SAs$  requires 8.84 c.c. Hence the purity was 95%).

*3'-Nitrobenzenesulphonyl-4-aminophenylarsinic Acid* (IV; *R* = H).—This acid was prepared from sodium *p*-aminophenylarsinate (1 mol.) and finely powdered nitrobenzenesulphonyl chloride (2 mols.) by the Fischer-Bergell method. The yield was 69% (Found: S, 7.7.  $C_{12}H_{11}O_7N_2SAs$  requires S, 8.0%). It is soluble in boiling 90% formic acid, and crystallises in short prisms, less readily in boiling acetic acid and very sparingly in boiling water. The maximum tolerated dose is 0.4 mg.

*3'-Aminobenzenesulphonyl-4-aminophenylarsinic Acid*.—The corresponding nitro-acid was reduced by ferrous chloride and alkali in the usual way at 0°, and the amino-acid isolated through its *magnesium* salt in hot ammoniacal solution. The yield was 70%. It is best purified as its *hydrochloride*, which is only moderately soluble in cold water and separates readily on addition of stronger acid in rhomb-shaped plates (Found: Cl, 8.5.  $C_{12}H_{13}O_5N_2SAs.HCl$  requires Cl, 8.7%). On addition of saturated sodium acetate solution to a warm concentrated solution of the hydrochloride, the *amino-arsinic acid* separates as a gum which rapidly crystallises, on rubbing, in long, narrow plates with sloping ends. It is moderately soluble in cold water. The maximum tolerated dose is 0.5 mg.

*3'-Aminobenzenesulphonyl-4-aminoarsenobenzene*.—This was prepared from the corresponding acid by means of hypophosphorous acid at 45–50° in the usual way (Found: As, 23.6.  $C_{24}H_{22}O_4N_4S_2As_2$  requires As, 23.3%). It is a white or creamy-white, amorphous powder when dry, soluble in sodium hydroxide, and slowly soluble in sodium carbonate solution. It dissolves in molten phenol, but the solution soon becomes turbid and finally fills with a finely-divided precipitate.

*3:3'-Dinitrobenzenesulphonyl-4-aminophenylarsinic Acid* (V; *R* = H).—*3'-Nitrobenzenesulphonyl-4-aminophenylarsinic acid* (10.0 g.) in 30 c.c. of sulphuric acid was slowly treated at 0° with nitric acid (1.75 c.c.; *d* 1.42) dissolved in a little sulphuric acid (5 c.c.). After 30 minutes, the solution was poured on to ice. The yield was 93%. This *dinitro-acid* crystallises well from boiling water, in which it is sparingly soluble, in short needles and similarly



from boiling 90% formic acid, in which it is readily soluble (Found : S, 7.2.  $C_{12}H_{10}O_9N_3SAs$  requires S, 7.2%). On boiling with 32% hydrochloric acid for 8 hours, it was only partly hydrolysed, giving an 83% yield of 3-nitro-4-aminophenylarsinic acid. No 4-aminophenylarsinic acid could be detected in the mother-liquors. The maximum tolerated dose is 0.1 mg.

3 : 3' - *Diaminobenzenesulphonyl-4-aminophenylarsinic Acid*.—Reduction of the corresponding dinitro-acid by ferrous chloride and alkali at 0° gave this *diamino-acid* in 70% yield. It was isolated through the magnesium salt in ammoniacal solution (Found : As, 19.5.  $C_{12}H_{14}O_5N_3SAs$  requires As, 19.4%). When liberated from acid solution by addition of sodium acetate, it crystallises in slightly distorted, diamond-shaped plates. The maximum tolerated dose is 1.5 mg.

3' - *Nitrobenzenesulphonyl-3-amino-4-hydroxyphenylarsinic Acid*.—3-Amino-4-hydroxyphenylarsinic acid (11.6 g.) was dissolved in water (60 c.c.) with the aid of 3.85 g. of anhydrous sodium carbonate. Nitrobenzenesulphonyl chloride (2 mols.; 22 g.) was added at once and a few drops of ether. The mixture was shaken for 30 minutes, and three successive portions of *N*-sodium carbonate (1 mol.) at 30-minute intervals were then added with intermediate shaking. The solution, on being made definitely acid to Congo-paper, deposited a pale-coloured gum immediately and, after 12 hours in the cold room, a crystalline powder. These were collected and stirred with 75 c.c. of *N*-hydrochloric acid in the boiling water-bath until the non-soluble portion had crystallised. This treatment was essential to remove aminohydroxyphenylarsinic acid carried down from acid solution with the gum. The crystalline, chalky solid obtained on cooling was a complex mixture probably containing *O*- and di-*N*-sulphonylated derivatives (Found : S, 9.0. A disulphonamide requires S, 10.6%). It was dissolved in 20 volumes of 0.5*N*-sodium hydroxide, boiled for 30 minutes, and while still hot treated with concentrated hydrochloric acid so long as an oily turbidity was produced. After brief stirring, the hot solution was freed from oil by filtration through a fluted paper. The filtrate showed no further tendency to deposit oil, but deposited the required nitro-acid in a crystalline state. The original mother-liquors on concentration under reduced pressure gave a succession of crops of the required nitro-acid and unchanged aminohydroxyphenylarsinic acid separable by extraction with *N*-hydrochloric acid. The total yield was 33%. If one molecular proportion of sulphonyl chloride was originally used instead of two, the same difficulties were encountered and the yield was 28%. For analysis, the *acid* was recrystallised from 20 volumes of boiling water, from which it crystallised extremely well

as a *dihydrate* in large, straw-coloured prisms or rhombs (Found : Loss at  $95^{\circ}$ , 8.4.  $C_{12}H_{11}O_8N_2SAs \cdot 2H_2O$  requires  $H_2O$ , 7.9%. Found on anhydrous material : S, 8.0.  $C_{12}H_{11}O_8N_2SAs$  requires S, 7.7%). When dissolved in sodium hydrogen carbonate solution and treated with a drop of dilute ferric chloride, it gives an intense purple solution which on addition of caustic alkali becomes redder ; the colour is discharged by excess of caustic alkali with separation of ferric hydroxide. On addition of acid, however, to neutrality to litmus, the colour is also discharged with precipitation of a grey, amorphous precipitate which, after separation, redissolves in sodium hydrogen carbonate solution with the same purple colour. In a similar way, cobalt nitrate gives a rose-coloured solution with an absorption band in the yellowish-green part of the spectrum. The reaction is more intense in sodium carbonate solution, but is discharged by excess of acid or caustic alkali. A nickel salt gives a clear yellowish-brown solution, whilst a copper salt gives an intense deep brown solution. The maximum tolerated dose is 0.5 mg.

*3'-Aminobenzenesulphonyl-3-amino-4-hydroxyphenylarsinic Acid.*—The reduction of the foregoing nitro-acid was carried out with ferrous chloride and alkali. The isolation of the pure amino-acid was effected as follows. The filtrate from the ferric hydroxide together with the alkaline extracts (0.2*N*-sodium hydroxide) of the ferric hydroxide was of a deep purple colour, and on being made neutral to Congo-paper deposited, after standing for 12 hours, the required amino-acid mixed with an amorphous, grey complex of ferric hydroxide and the amino-acid. These were collected, dissolved in 2*N*-sodium hydroxide, and filtered from the ferric hydroxide, which separated in part. The filtrate, on being made neutral to litmus, deposited the remainder of the bound iron as the complex, which could be removed, and thereafter the pure amino-acid was obtained on making the filtrate neutral to Congo-paper. The iron complex could be re-submitted to the same treatment with caustic alkali, when ferric hydroxide was again precipitated, but not quite completely, and the filtrate gave a further small crop of iron complex and the pure amino-acid on being made neutral to litmus and Congo-paper, respectively. The original mother-liquors, on concentration under reduced pressure, yielded further crops of pure amino-acid. For physiological testing and analysis, the combined crops of amino-acid were dissolved in *N*-hydrochloric acid and precipitated with saturated sodium acetate solution. The yield was 76% (Found : Loss at  $95^{\circ}$ , 7.5 ; S, 7.5.  $C_{12}H_{13}O_6N_2SAs \cdot 2H_2O$  requires  $H_2O$ , 8.1 ; S, 7.6%). It crystallises from boiling water, in which it is fairly readily soluble, in glistening prisms. It is readily soluble in *N*-hydro-

chloric, nitric, or sulphuric acid. The *hydrochloride* crystallises in rectangular tablets, the *sulphate* in short needles, and the *nitrate* in prisms. In sodium hydrogen carbonate solution, the amino-acid gives a purple colour with ferric chloride and on neutralisation to litmus a complex containing iron is precipitated as a dove-grey powder. Some preparations, however, are almost black. This is free from chloride and dissolves in sodium hydrogen carbonate with restoration of the purple colour (Found on air-dried material: Fe, 10.4; S, 6.5, whence  $\text{Fe} : \text{S} = 1 : 1.08$ ). The rose-pink colour developed on similar addition of cobalt nitrate is very marked. There is an absorption band in the yellowish-green. A soluble nickel complex is similarly formed with a yellowish-brown colour, and with copper salts a very intense brownish-red solution is obtained showing considerable stability to caustic alkali. The maximum tolerated dose is 0.5 mg.

*3'-Nitrobenzenesulphonyl-4-amino-2-hydroxyphenylarsinic Acid.*—4-Amino-2-hydroxyphenylarsinic acid (11.6 g.) was converted into the sulphonamide by the Fischer-Bergell process, nitrobenzenesulphonyl chloride (2 mols.) being used. The solution, on being made acid to Congo-paper, deposited a gum and, on standing some hours, a crop of crystals. The total precipitate was collected and warmed on the water-bath with *N*-hydrochloric acid; it then became wholly crystalline. It was dissolved in 10 volumes of *N*-sodium hydroxide and heated on the water-bath for 30 minutes. The *nitro-acid* was obtained on acidification in colourless needles rapidly transforming to plates; yield 9.1 g. The original mother-liquors contained additional acid, which was isolated by concentration. This acid is a dihydrate (Found: Loss at  $95^\circ$ , 8.4.  $\text{C}_{12}\text{H}_{11}\text{O}_8\text{N}_2\text{SAs} \cdot 2\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 8.2%. Found on anhydrous material: S, 8.0, 7.6.  $\text{C}_{12}\text{H}_{11}\text{O}_8\text{N}_2\text{SAs}$  requires S, 7.7%). It is soluble in 32 parts of boiling water and separates in very pale buff-coloured rhombs or prisms. (For its colour reactions, see next paragraph.) The maximum tolerated dose is 0.2 mg.

*3'-Aminobenzenesulphonyl-4-amino-2-hydroxyphenylarsinic Acid.*—This acid was prepared from the nitro-acid in 63% yield by means of ferrous chloride and alkali. It tends to form an iron complex in the alkaline extracts of the ferric hydroxide precipitate just as does its isomeride described above. It can be isolated, however, in exactly the same way (Found: S, 8.1.  $\text{C}_{12}\text{H}_{13}\text{O}_6\text{N}_2\text{SAs}$  requires S, 8.3%). It is readily soluble in boiling water and crystallises in tufts of fine needles. In *N*-mineral acids it is very readily soluble. When dissolved in sodium hydrogen carbonate solution, it gives a clear deep yellowish-brown colour with ferric chloride and a bright emerald-green colour with copper sulphate. Under comparable

conditions, the parent nitro-acid gives with ferric chloride a clear reddish-brown solution and with copper salts an olive-green solution. The parent acid of this group, 4-amino-2-hydroxyphenylarsinic acid, gives a reddish-brown solution with ferric salts and an emerald-green solution with copper sulphate. The maximum tolerated dose is 0.025 mg.

*N-p-Toluenesulphonyl-o-aminophenol* (VIII;  $R = H$ ).—When prepared by the process described by Reverdin and de Luc (*Ber.*, 1914, 47, 1538) for the isomeric derivative of *m*-aminophenol, this sulphonamide was obtained in very good yield and agreed in properties with the description given by Tröger and Ullmann (*J. pr. Chem.*, 1895, 51, 441). It dissolves on warming with dilute aqueous sodium carbonate; the solution becomes turbid on cooling and gives a bright purple colour on addition of ferric chloride. With cobalt nitrate, it gives a pink colour with an absorption band in the yellow-green.

*N-p-Toluenesulphonyl-o-methylaminophenol* (IX) was prepared by extending Reverdin and de Luc's method to *o*-methylaminophenol. *o*-Methylaminophenol sulphate ("Ortol," 4.3 g.) and sodium acetate (6.8 g.; hydrated) were dissolved in 50% alcohol (100 c.c.) and heated for 30 minutes on the water-bath, *p*-toluenesulphonyl chloride (4.75 g.) being added in several portions from time to time. On cooling, *N-p-toluenesulphonyl-o-methylaminophenol* (4.6 g.) separated in white needles. It was recrystallised from glacial acetic acid and showed m. p. 127—128° (Found: S, 11.3.  $C_{14}H_{15}O_3NS$  requires S, 11.6%). It is readily soluble in caustic alkali but insoluble in dilute acids. It is unchanged by nitrous acid. Its solution in boiling dilute aqueous sodium carbonate becomes turbid on cooling, but gives no purple colour with ferric chloride and no pink colour with cobalt nitrate.

*N-4-Toluenesulphonyl-3-amino-4-hydroxybenzoic Acid* (VIII;  $R = CO_2H$ ).—Aminohydroxybenzoic acid (1.5 g.) was dissolved in 10 c.c. of pyridine and treated with 2.37 g. of toluenesulphonyl chloride. After 12 hours, the mixture was poured into *N*-hydrochloric acid, the solid collected, and boiled for 30 minutes with *N*-sodium hydroxide. On acidification the sulphonamide separated straightway almost pure in 77% yield. For analysis it (2.3 g.) was recrystallised from the minimum volume (50 c.c.) of 50% (by vol.) acetic acid and separated in glistening, pale straw-coloured, wedge-shaped prisms, m. p. 250° (decomp.) (Found: S, 10.7.  $C_{14}H_{13}O_5NS$  requires S, 10.4%). In sodium hydrogen carbonate solution it gives an intense purple colour with ferric chloride and a bright pink colour with cobalt nitrate, the solution showing an absorption band in the yellowish-green part of the spectrum.

*N-p-Toluenesulphonyl-p-methylaminophenol* was prepared following Reverdin's directions for his so-called *O-toluenesulphonyl-N-p-monomethylaminophenol*. It melts at 136–137° (Reverdin gives 135°) and crystallises in needles from dilute alcohol or benzene. It is insoluble in dilute acids and unchanged by nitrous acid, but is readily soluble in sodium hydroxide and in sodium carbonate solution on warming. When dissolved in sodium carbonate solution, it does not give a coloration with ferric chloride.

*p-Xanthylphenylarsinic Acid* (XII).—Sodium *p*-aminophenylarsinate pentahydrate (32.9 g.) was diazotised at 0° in 200 c.c. of water and 30 g. of concentrated hydrochloric acid, and the product run slowly into a rapidly stirred solution of 20 g. of potassium xanthate in 420 c.c. of a 10% solution of hydrated sodium carbonate, kept at 80°. After being stirred for 1 hour, the solution was cooled and acidified. The precipitated resin solidified after a few hours and was submitted to a partial purification by dissolution in sodium carbonate solution, filtration from insoluble by-products, and reprecipitation by acids. The yield of crude xanthate was 62% (Found: S, 18.8.  $C_9H_{11}O_4S_2As$  requires S, 19.9%). The acid could not be obtained crystalline nor of a higher sulphur content, but it behaved normally on oxidation.

*Oxidation of p-Xanthylphenylarsinic Acid*.—Five g. of crude *p*-xanthylphenylarsinic acid were heated on the water-bath for 2 hours with 100 c.c. of 3*N*-nitric acid and finally to boiling for  $\frac{1}{2}$  hour. When cold, the crystalline acid was collected (yield 82%). *Diphenyl disulphide pp'-diarsinic acid* (XIII) dissolves in 900 parts of boiling water, from which it crystallises in narrow plates or needles. It crystallises much more readily from 200 parts of 2*N*-nitric acid (Found: As, 32.2; S, 13.9.  $C_{12}H_{12}O_6S_2As_2$  requires As, 32.2; S, 13.8%). A 1% solution in 0.2*N*-ammonia treated with 5% barium chloride solution gave, on heating, a *barium* salt crystallising in needles. On cooling, the barium salt rapidly re-dissolved, but was again precipitated on heating. The acid has a maximum tolerated dose of 0.002 mg.

The nitric acid mother-liquors of the above oxidation were evaporated to a syrup with repeated additions of water to remove the excess of nitric acid. They were then diluted and treated with sufficient baryta to precipitate the sulphuric acid present. On evaporation the solution set to a crystalline magma of *p-sulphophenylarsinic acid* (XIV). This was redissolved in water, and the solution evaporated until a crust formed. On keeping, the acid separated in long prisms. These are extremely soluble in water, but can be freed from the mother-liquors by washing with glacial acetic acid. The whole of the *p*-xanthylphenylarsinic acid unaccounted

for as disulphide appears to be present as sulpho-acid. The sulpho-acid was, however, more readily obtained as follows. The disulphide (5 g.) was boiled with 50 c.c. of 6*N*-nitric acid for 4 hours. The clear solution was evaporated dry and left 6.0 g. of crude sulpho-arsinic acid. This was crystallised once from water and washed with glacial acetic acid (Found: Loss at 95°, 5.8.  $C_6H_7O_6SAs.H_2O$  requires  $H_2O$ , 6.0%. Found on anhydrous material: S, 11.6.  $C_6H_7O_6SAs$  requires S, 11.4%). This acid also crystallises occasionally in hexagonal plates, possibly an anhydrous form, as it frequently appears as a crust on the surface of hot saturated solutions. The maximum tolerated dose is 0.5 mg.

The disulphide is reduced by hypophosphorous acid in the presence of a trace of iodide to an insoluble, yellow arseno-compound, probably *thiolarsenobenzene*, because it is insoluble in sodium hydrogen carbonate but soluble in caustic alkali. Under similar conditions, at 50–55° *p*-sulphophenylarsinic acid is reduced to *p*-sulphophenylarsenobenzene, which is very soluble in water and can be isolated in a crude condition as a yellow, gelatinous product by evaporation of the reduction liquors in a vacuum over sulphuric acid.

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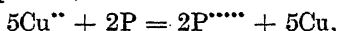
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## CLXXVII.—*The Action of Phosphorus on Salts of Silver and Other Metals.*

By OSWALD JAMES WALKER.

It has long been known that yellow phosphorus is able to precipitate many heavy metals from solutions of their salts, and attempts have been made to obtain quantitative information about the phenomenon by determining the ratio of metal deposited to phosphorus which had reacted. Using solutions of copper sulphate, Straub (*Z. anorg. Chem.*, 1903, **35**, 460) investigated the ratio of the amount of copper deposited to the total amount of phosphorus which had reacted (*i.e.*, phosphorus as phosphide and phosphoric acid), but he did not obtain any definite value. He concluded that the action proceeded in stages, and that when it was incomplete or when atmospheric oxygen was rigorously excluded 1 atom of phosphorus precipitated 2 atoms of copper. Tauchert (*Z. anorg. Chem.*, 1913, **79**, 350) obtained similar results, but stated that hypophosphoric acid was one of the products. Bird and Diggs (*J. Amer. Chem. Soc.*, 1914, **36**, 1382) also investigated the action of phosphorus on copper sulphate and concluded that the main

action consisted in the transfer of positive charges from the copper ions to the phosphorus, as follows :



the positive phosphorus ions reacting immediately with water to form phosphoric acid. In support of their theory, Bird and Diggs found that the ratio of atoms of copper precipitated to phosphorus oxidised to phosphoric acid was approximately 5 : 2. In obtaining this ratio, however, they did not include the amount of phosphorus present as lower acids and as phosphide. They ascribed these products to secondary reactions.

#### EXPERIMENTAL.

In order to determine to what extent phosphorus reacts with solutions of salts of the heavy metals and to decide which metal would be most suitable for a more detailed investigation, sticks of phosphorus were kept in contact with solutions of salts of a large number of different metals. Deposits of metallic appearance were found on the surface of the phosphorus after varying intervals with neutral or slightly acid solutions of salts of the following metals—gold, platinum, palladium, silver, mercury, and copper. No action was observed, even after several weeks, with salts of metals below copper in the electrochemical series, provided that the solution was not alkaline. In ammoniacal solution, however, salts of the following metals also gave deposits on the surface of the phosphorus—lead, nickel, thallium, and, not quite so readily, tin, cobalt, cadmium, and zinc. An interesting point of considerable importance is revealed by comparing these results with the data which are available for the action of phosphine on metallic salt solutions in papers by Kulisch (*Annalen*, 1885, **231**, 327), Moser and Brukl (*Z. anorg. Chem.*, 1922, **121**, 73), and Brukl (*ibid.*, 1922, **125**, 252). An examination of their results shows that those solutions which react with phosphine are exactly those which give deposits on phosphorus, and the metals may be divided into the same two groups mentioned above with respect to the action of phosphine on their salt solutions. Reference to this point will be made at a later stage.

From the above experiments, the most suitable salts for a more detailed investigation seemed to be those of silver and copper. As silver salts had not been used previously in any quantitative study, it was decided to examine more closely the action of phosphorus on them and especially on the nitrate. There is no possibility in this case of the metal being reduced to a lower stage of valency, and, as will be shown below, the complications due to the

formation of phosphide are not so great as with copper salts. In order to minimise any oxidising effect due to the free nitric acid formed, concentrations not greater than  $N/10$  were used as a rule.

*Action of Yellow Phosphorus on Silver Salts.*

The phosphorus used throughout the course of this work was purified by warming with caustic soda solution, then with potassium dichromate and sulphuric acid, followed by thorough washing. It was cast into thin sticks and kept under water in the dark.

When a stick of phosphorus was placed in a  $N/10$ -solution of silver nitrate, a black, shiny deposit was formed almost immediately on the surface of the phosphorus; bright crystalline silver was then slowly deposited which finally became grey and spongy when it was all out of solution. After complete deposition of the silver, the solution contained phosphoric, phosphorous, and nitric acids, and traces of nitrous acid. No hypophosphorous acid, hypophosphoric acid, or ammonia was detected. The deposit consisted almost entirely of metallic silver, but contained a small amount of phosphorus, due to a thin, darker layer next to the surface of the phosphorus stick. This thin layer appeared to be a phosphide of silver and was probably the same as the black deposit first formed when the phosphorus was placed in the silver nitrate solution. The amount of phosphorus present in the deposit was small compared with that in the solution as oxy-acids. The question of phosphide formation will be considered later.

With solutions of silver sulphate and of silver acetate the reaction proceeded in a similar way. When phosphorus was placed in an ammoniacal solution of silver nitrate, a black deposit was formed which was converted, after some time, into white, crystalline silver. With a solution of silver cyanide in potassium cyanide a black deposit was very slowly formed on the surface of the phosphorus.

*Quantitative Experiments with Silver Salts.*—Experiments were made in the first place to determine whether any definite relationship existed between the amount of silver deposited and the total amount of phosphorus oxidised. Preliminary determinations showed that the ratio of the number of atoms of silver precipitated to the number of atoms of phosphorus oxidised, denoted hereafter as  $Ag : P$ , varied with the length of time during which the phosphorus had remained in contact with the solution. Accordingly, the ratio  $Ag : P$  was determined before complete precipitation of the silver had taken place.

Sticks of phosphorus were placed in solutions of silver nitrate, and portions withdrawn at intervals for the determination of the



amounts of silver salt and of phosphorus acids in the solution. The silver was determined in one portion by Volhard's method. A second portion was evaporated to dryness with aqua regia in order to ensure complete oxidation of the phosphorous acid, and the phosphoric acid was determined gravimetrically as magnesium pyrophosphate. In later experiments, this method was replaced by the more convenient volumetric method of Wilkie (*J. Soc. Chem. Ind.*, 1910, **29**, 794), in which the phosphoric acid was precipitated under given conditions as silver phosphate by means of standard silver nitrate solution, the excess of silver nitrate being titrated with thiocyanate solution after filtering.

TABLE I.

Expt.	AgNO <sub>3</sub> .	Time (hrs.).	Ag pptd. (= a).	P oxid. (= b).	Ag : P (= a/b).	$\frac{a-a_0}{b-b_0}$ .
1	0.1008	19	0.0279	0.00588	4.74	—
		48	0.0764	0.01810	4.22	4.0
		55	0.0904	0.02207	4.10	3.9
		61	0.1008	0.02836	3.55	—
2	0.1000	24	0.0190	0.00367	5.18	—
		48	0.0704	0.0156	4.51	4.3
		54	0.0846	0.0197	4.29	4.1
		59	0.0975	0.0236	4.13	3.9
		72	0.1000	0.0303	3.29	—
3	0.1000	16.5	0.0112	0.00204	5.49	—
		24	0.0210	0.00428	4.91	(4.4)
		41	0.0608	0.01419	4.29	4.1
		65	0.0996	0.02686	3.70	3.6
4	0.1000	16.5	0.0120	0.00243	4.94	—
		24	0.0228	0.00470	4.85	(4.8)
		41	0.0624	0.01472	4.24	4.1
		65	0.1000	0.02826	3.54	—
5	0.502	—	0.1060	0.0187	5.66	—
		—	0.1555	0.0305	5.09	4.2

The results of several experiments with solutions of silver nitrate are in Table I, all concentrations being given in g.-atoms or g.-mols. per litre. The general conclusions may be summarised as follows :

1. The ratio Ag : P varied during the deposition of the silver from a value of more than 5 : 1 near the beginning of the reaction to about 3.6 : 1 at the point corresponding to complete deposition of the silver.

2. No appreciable oxidation of the phosphorus by the oxy-acid set free from the metallic salt took place. Experiments in which solutions of the sulphate were used, in order to avoid the formation of nitric acid, gave results similar to those obtained with the nitrate solutions.

3. The phosphorus was not appreciably oxidised by atmospheric oxygen. Similar results were obtained whether air was bubbled through the solution (Expt. 3) or completely excluded (Expt. 4) during the deposition of the silver.

4. The oxygen necessary for the oxidation of the phosphorus must therefore come from the decomposition of the water.

A further slow oxidation of the phosphorus took place even after complete precipitation of the silver. This is shown by the results in Table II. In these experiments equal quantities of a standard silver nitrate solution were sealed up with phosphorus sticks in small bulbs. After sufficient time had elapsed to allow all the silver to be deposited, the bulbs were opened at varying intervals and the total phosphorus acids were determined in the solution. It will be seen that the quantity of phosphorus oxidised increases with the time, and that the values of the ratio Ag : P are much lower than those obtained before complete precipitation of the silver.

TABLE II.

Expt.	Time (days).	Ag pptd.	P oxid.	Ag : P.
1	6	0.00250	0.000717	3.49
	9		0.000807	3.10
	14		0.000865	2.89
2	7	0.00277	0.000857	3.23
	17		0.00120	2.31

The points obtained by plotting against one another the values of silver precipitated and phosphorus oxidised before complete precipitation of the silver lie approximately on a straight line which corresponds to a constant ratio of Ag : P of 4 : 1 but which does not pass through the origin. The ratio Ag : P calculated from the actual values of silver precipitated and phosphorus oxidised has, on the other hand, been shown to decrease with time. If, however, the ratio Ag : P is calculated by taking, not the values of total silver precipitated and total phosphorus oxidised from the beginning of the reaction, but the differences between subsequent values and the first value ( $a_0$  or  $b_0$ ) in each experiment, a much more constant ratio Ag : P is obtained, as shown in the last column of Table I. The average value is 4.0 : 1, if the two values shown in brackets, which are obtained from small differences, are neglected.

It would appear, therefore, that whilst at the beginning of the reaction the ratio Ag : P is higher than 4 : 1, after a certain time the main reaction taking place corresponds approximately to the precipitation of 4 atoms of silver for every atom of phosphorus oxidised.

*Formation of Phosphorous Acid.*—It was thought desirable to examine whether any definite relationship existed between the amounts of silver deposited and of phosphorous acid formed. Bird and Diggs supposed that the formation of phosphorous acid was due to the reduction of the phosphoric acid by the excess of

phosphorus, but this is most improbable. The further reaction between the phosphorous acid formed and the silver nitrate still in solution would, of course, introduce a complication, but experiments made to test this reaction showed that it was negligible in the concentrations used.

Phosphorus sticks were placed in solutions of silver nitrate and the amounts of phosphorous acid and of silver salt in the solution were determined at intervals. Phosphorous acid was estimated by the iodimetric method of Boyer and Bauzil (*J. Pharm. Chim.*, 1918, 18, 321), after the excess of silver salt had been precipitated with potassium iodide. The results of several experiments are in Table III.

TABLE III.

Expt.	AgNO <sub>3</sub> .	Ag pptd. (= a).	% of total Ag pptd.	H <sub>3</sub> PO <sub>3</sub> (= b).	Ag : H <sub>3</sub> PO <sub>3</sub> (= a/b).	$\frac{a-a_0}{b-b_0}$ .
1	0.10	0.0704	70	0.01070	6.6	—
		0.0846	85	0.01286	6.6	6.6
		0.0975	98	0.01496	6.5	6.4
2	0.10	0.0099	9.9	0.00124	8.0	—
		0.0323	32	0.00488	6.6	6.2
		0.0420	42	0.00654	6.4	6.1
		0.0492	49	0.00770	6.4	6.1
		0.0988	99	0.01638	6.0	5.9
3	0.481	0.0695	14	0.00804	8.7	—
		0.0850	17	0.01038	8.2	6.6
		0.1240	25	0.01618	7.7	6.7
		0.425	85	0.0619	6.9	6.4
4	0.502	0.0755	15	0.00676	11.2	—
		0.0825	16.5	0.00794	10.5	5.9
		0.0910	18.4	0.00922	10.0	6.3

With *N*/10-solutions, the ratio of silver precipitated to phosphorous acid formed (Ag : H<sub>3</sub>PO<sub>3</sub>) is fairly constant, with the exception of one determination which was made near the beginning of the reaction. In Expts. 3 and 4, *N*/2-silver nitrate was used and determinations of the ratio Ag : H<sub>3</sub>PO<sub>3</sub> were made before 25% of the total silver had been precipitated. The results are higher and not constant. If, however, the values of silver precipitated and phosphorous acid formed are plotted against one another, the points lie on straight lines having a slope corresponding to a constant ratio of Ag : H<sub>3</sub>PO<sub>3</sub> of 6.3 : 1. By subtracting in each experiment the first values of silver deposited (*a*<sub>0</sub>) and of phosphorous acid formed (*b*<sub>0</sub>) from the subsequent values, and by using these differences to calculate the ratio Ag : H<sub>3</sub>PO<sub>3</sub>, fairly constant figures are obtained, as is shown in the last column of Table III.

From the quantitative experiments already mentioned, it would appear that phosphorous and phosphoric acids are produced simultaneously in constant proportion during the action of phosphorus

on silver nitrate, if we neglect the first stages of the reaction. In the following table are the results of an experiment in which the phosphorous acid and the total oxidised phosphorus ( $\text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$ ) were determined in a solution of silver nitrate in contact with phosphorus, at varying intervals before the silver was completely precipitated.

TABLE IV.

$\text{H}_3\text{PO}_3 (= a).$	$\text{H}_3\text{PO}_3 + \text{H}_3\text{PO}_4$ ( $= b$ ).	$a/b.$	$\frac{a-a_0}{b-b_0}.$
0.00318 ( $= a_0$ )	0.00367 ( $= b_0$ )	0.87	—
0.0107	0.0156	0.69	0.63
0.0129	0.0197	0.65	0.60
0.0150	0.0236	0.63	0.59

The figures in the third column show, however, that near the beginning of the reaction phosphorous acid is the chief product formed.

*Electrochemical Nature of the Reaction between Phosphorus and Metallic Salt Solutions.*

Wöhler (*Annalen*, 1851, **79**, 126) found that when phosphorus was placed in a solution of copper sulphate, copper was deposited on a copper wire in contact with the phosphorus. Wicke (*ibid.*, 1852, **82**, 145) likewise noticed that silver was deposited on the surface of a silver wire in contact with phosphorus placed in silver nitrate solution; and Bird and Diggs (*loc. cit.*) described similar experiments which they regarded as evidence strongly in favour of their electrochemical theory.

Experiments were made to determine whether deposition of metal would take place on any conducting surface in contact with the phosphorus. Platinum, gold, silver, and carbon were kept in contact with phosphorus sticks immersed in solutions of silver nitrate or of copper sulphate. In every case silver or copper was deposited on the conducting surface at points far removed from the phosphorus. No metal was deposited on non-conducting surfaces in contact with the phosphorus, such as glass, or on a conducting surface which did not touch the phosphorus.

These experiments suggest that an action of an electrochemical nature is taking place and this is shown more clearly by the following experiment. A stick of phosphorus was fused on to a platinum wire and placed in a porous pot containing *N*/10-silver nitrate and standing in a beaker filled with silver nitrate of the same concentration. The free end of the platinum wire was bent over so as to make metallic connexion between the inner and outer solutions. Silver was deposited on the phosphorus and on the platinum

wire in the inner solution, and after some time the platinum wire dipping into the outer solution was covered with a bright deposit of crystalline silver. Silver was also deposited on the outer wall of the porous diaphragm at points which had apparently no metallic connexion with the platinum wire or with one another. In experiments in which no platinum wire was used, a stick of phosphorus alone being placed in the inner solution, deposition of silver again took place on the outer wall of the porous cell. This was found to be due to silver being deposited in the pores of the diaphragm, thus establishing metallic connexion between the inner and outer solutions. Deposition of silver on the outer wall of the diaphragm took place only when the inner wall was in metallic connexion with the phosphorus. Similar results were obtained by using solutions of silver sulphate or silver acetate.

In all these experiments metal ions were discharged and metal deposited—in some cases at a considerable distance from the surface of the phosphorus—only at such points as were in metallic connexion with the phosphorus surface, the contact being established either by the metal already deposited or by another conductor. The physical state of the silver and copper deposited by means of phosphorus in these experiments strongly resembled the state in which these metals are deposited from their salt solutions by an electric current. These facts favour the view that an action of an electrochemical nature takes place, *i.e.*, a direct discharge of ions to the metallic state.

#### *Formation of a Phosphide.*

The quantitative results show that owing to the formation of a phosphide in the early stages of the reaction the precipitation of the silver is not accompanied by the oxidation of an exactly equivalent amount of phosphorus. It was not found possible to ascertain the constitution of the phosphide formed, but indirect evidence indicates the probability that it is the compound  $\text{Ag}_3\text{P}$ . Moser and Brukl (*Z. anorg. Chem.*, 1922, **121**, 80) obtained this compound by the action of phosphine on silver nitrate solution and showed that it was an unstable substance capable of reacting with an excess of silver salt to give metallic silver and acids of phosphorus. The phosphide obtained by the action of phosphorus on silver nitrate was likewise decomposed by excess of silver salt. The deposit obtained by keeping a stick of phosphorus in silver nitrate solution for a short time was separated from the phosphorus, washed, and placed in *N*/10-silver nitrate. Ten c.c. of this solution, immediately after introduction of the silver deposit, were equivalent to 9.85 c.c. of a thiocyanate solution. After a few days,

10 c.c. required only 9.05 c.c. of the thiocyanate, and the solution gave a precipitate with ammonium molybdate, thus showing that silver had been precipitated and phosphorus oxidised.

The work of Christomanos (*Z. anorg. Chem.*, 1904, **41**, 309) on the action of phosphorus dissolved in ether or in benzene on solutions of copper salts pointed to the formation of a phosphide having the formula  $\text{Cu}_3\text{P}_2$ . In the case of silver salts, a black phosphide was formed, but no definite compound was isolated. Experiments were made to determine the constitution of the phosphide obtained by shaking a solution of silver nitrate with solutions of phosphorus in ether, benzene, and carbon disulphide. The black precipitate so obtained became greyer in colour after standing in contact with excess of silver salt, and it gradually assumed the appearance of metallic silver. The proportion of silver to phosphorus in the black precipitate first formed varied considerably owing to the difficulty in washing it free from excess of phosphorus without causing decomposition. The values obtained for the ratio Ag : P in the washed, but damp, precipitate varied between 2.5 : 1 and 3.9 : 1. It seems probable that, in this case also,  $\text{Ag}_3\text{P}$  is formed.

After a solution of silver nitrate had been shaken with a solution of phosphorus, the aqueous layer always contained phosphorous and phosphoric acids. The ratio of silver precipitated to phosphorus oxidised was determined. In the early stages, when the precipitate was quite black and consisted almost entirely of phosphide, high values of the order of 10 : 1 were obtained for the ratio Ag : P. When the mixture had stood for several days until the precipitate appeared to consist wholly of metallic silver, the ratio Ag : P lay between 5 : 1 and 3 : 1, i.e., the values were of the same order as those obtained in the experiments with phosphorus sticks. The presence of phosphorous acid in the above experiments was due to the first reaction, viz., the formation of phosphide. Silver phosphide, prepared by the action of phosphine or of solutions of phosphorus in various solvents, was washed and placed in a fresh quantity of silver nitrate solution. The phosphide was slowly oxidised to silver and phosphoric acid, no phosphorous acid being produced.

#### *Action of Phosphorus on Solutions of Copper Salts.*

The amount of phosphide formed in the case of copper salts was quite appreciable. Experiments with *N*/10-copper sulphate showed that, at the point corresponding to complete precipitation of the copper, about 13% of the total phosphorus which had reacted was present as phosphide, the remainder being in the solution as phosphorous and phosphoric acids. In the case of silver

salts, practically all the phosphorus which had reacted was present in the solution as oxy-acids.

If, however, the stick of phosphorus covered with the deposit of phosphide and copper was kept in contact with the solution for a long period, more phosphorus was oxidised, even if atmospheric oxygen was excluded, and eventually no phosphide was left in the deposit. This disposes of the suggestion of Bird and Diggs, who stated that the bright deposit of copper on remaining in contact with the phosphorus was gradually converted, as a secondary reaction, into the black phosphide. In the case of copper precipitated from a solution of the sulphate, the deposit was certainly found to turn black on standing, but it then contained no phosphorus. The deposit obtained from copper nitrate solutions retained its bright coppery colour for months. The experimental evidence shows that the phosphide formation takes place between phosphorus and metal ions, and not between phosphorus and the metal.

A determination was made of the ratio between the amounts of copper precipitated and of phosphorus oxidised before complete precipitation of the metal, the procedure being the same as in the case of silver nitrate. *N*/10- and *N*/2-Solutions of copper sulphate and copper nitrate were used. Copper was estimated in the solution volumetrically by means of thiosulphate solution. The values of copper precipitated and of phosphorus oxidised, expressed in g.-atoms per litre, are in Table V, the concentrations of copper salts being expressed in g.-mols. per litre.

TABLE V.

Expt.	Cu salt.	Time (hrs.).	Cu pptd. (= <i>a</i> ).	P oxid. (= <i>b</i> ).	Cu : P (= $2a/b$ ).	$\frac{a-a_0}{b-b_0} \times 2$ .
1	0.05	39	0.0351	0.0145	4.8	—
	CuSO <sub>4</sub>	47	0.0394	0.0170	4.6	3.8
		69	0.0470	0.0209	4.5	3.8
2	0.05	39	0.0319	0.0135	4.7	—
	Cu(NO <sub>3</sub> ) <sub>2</sub>	47	0.0361	0.0156	4.6	4.1
		69	0.0445	0.0199	4.5	3.9
3	0.25	48	0.1523	0.0622	4.9	—
	CuSO <sub>4</sub>	88	0.2407	0.1051	4.6	4.1
4	0.25	40	0.1437	0.0549	5.2	—
	Cu(NO <sub>3</sub> ) <sub>2</sub>	88	0.2483	0.1115	4.5	3.7

The values of the ratio Cu : P have all been multiplied by 2 in order to make them comparable with the values of Ag : P. It will be seen that the value of Cu : P depends on the extent to which the reaction has proceeded. If, however, this ratio is calculated as shown in the last column, the disturbing effect of phosphide formation near the beginning is avoided and more constant values are obtained. As in the case of silver nitrate, after the reaction

between phosphorus and the metallic salt has proceeded for some time, 1 atom of phosphorus is oxidised for every 4 equivalents of the metal deposited.

### *Discussion and Summary.*

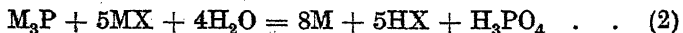
From the experiments with silver and copper salts it appears that when a stick of phosphorus is placed in a solution of the metallic salt solution a reaction proceeds in two distinct stages. The first process is the formation of a black phosphide on the surface of the phosphorus; at the same time, the solution is found to contain phosphorous acid. After a layer of the phosphide has been formed, metal begins to be deposited in a bright crystalline state, and phosphorus is oxidised to phosphorous and phosphoric acids. During this stage, approximately 4 equivalents of the metal are deposited for every atom of phosphorus oxidised.

With regard to the formation of a phosphide, there can be little doubt that it is due to the prior production of phosphine by the action of phosphorus on water, another portion of the phosphorus being simultaneously oxidised to phosphorous acid. Strong evidence for this view is obtained from the exact parallelism which exists between the actions of phosphorus and phosphine on salt solutions of the heavy metals; only those metallic salt solutions which give phosphides by the action of phosphine are able to react with phosphorus. Cross and Higgins (J., 1879, 35, 255) found that boiling water was decomposed by phosphorus, which was partly reduced to phosphine and partly oxidised to oxy-acids, and that, in the absence of oxygen, decomposition of the water took place only in the presence of certain metallic salts.

It is suggested, therefore, that the first stage in the action of phosphorus on the metallic salt takes place as follows (M and X representing an equivalent of the positive and negative radicals, respectively) :



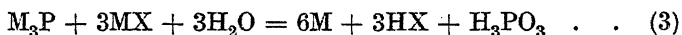
The appearance of a deposit of the metal evidently depends on the preliminary formation of the phosphide. It has already been shown that the phosphides of silver and of other metals are capable of reacting with excess of the metallic salt to give the metal and phosphoric acid. The second stage, therefore, appears to be



According to these equations, 4 equivalents of the metal should be deposited for every atom of phosphorus oxidised, and this was the ratio actually obtained with silver and copper salts. The



amount of phosphorous acid, however, was somewhat greater than that required by these equations. It is quite possible that this may be due to the following reaction proceeding to a small extent along with reaction (2) :



As regards the phenomena which have been described as electro-chemical, it must be assumed that reaction (2) is responsible for their appearance. This reaction consists essentially in the discharge of positive metal ions while phosphorus becomes oxidised, *i.e.*, loses electrons. The ionic process may be represented as  $\text{M}_3\text{P} + 5\text{M}' = 8\text{M} + \text{P}^{\text{*****}}$ , the positive phosphorus ions reacting immediately with water to form phosphoric acid. According to this view, the  $\text{P}^{\text{*****}}$  ions constitute an intermediate stage in the transition from phosphide to phosphoric acid. The discharge of  $\text{M}'$  ions and the formation of  $\text{P}^{\text{*****}}$  ions may occur at points widely separated from one another, provided that a metallic conducting path be available for the passage of the necessary electrons.

In conclusion, I wish to thank Professor Sir James Walker, F.R.S., for his interest and helpful advice during the course of this work.

UNIVERSITY OF EDINBURGH.

[Received, March 10th, 1926.]

## CLXXVIII.—*Experiments on the Formation of Mother-of-Pearl.*

By PHANI BHUSAN GANGULY.

It is known that mother-of-pearl, like the substance of the pearl, consists of calcium carbonate associated with water and an organic substance (conchiolin). The following is a typical analysis of mother-of-pearl (G. and H. Harley, *Proc. Roy. Soc.*, 1888, **43**, 461): Calcium carbonate, 66.0; organic matter, 2.5; water, 31.0%; total 99.5%.

As early as 1814, Brewster (*Phil. Trans.*, 1814, **104**, 397) explained the iridescent colours of mother-of-pearl as being due to two factors—a grating effect on the surface, and an interference effect caused by a thin film of calcium carbonate. The grating effect on mother-of-pearl can be easily transferred to a film of gelatin dried on its surface, and the distance between the lines can be measured. In a recent paper, Lord Rayleigh (*Proc. Roy. Soc.*, 1923, *A*, **102**, 674) has shown that the second effect is not due to a single film, but is caused by alternate layers of calcium carbonate and conchiolin, forming a series of equally spaced thin parallel plates. He ascribes the surface effect to the edges of the closely packed alternate layers

of inorganic and organic matter. This alternating structure is suggestive of the periodic precipitations which occur in the well-known Liesegang phenomenon, and as a matter of fact both Liesegang (*Kolloid Z.*, 1913, **12**, 181) and Clément and Rivière (*Compt. rend.*, 1922, **174**, 1353) have tried to produce structures similar to mother-of-pearl by the periodic precipitation of calcium phosphate in gelatin. Thus Liesegang allowed sodium phosphate to diffuse from an aqueous solution into a gelatin jelly containing calcium nitrate. The periodic structures obtained in this way exhibit some iridescence, but after a time they lose their lustre and become dull and "chalky." In order to avoid effects due to foreign electrolytes, it was decided to study the precipitation of calcium carbonate from an aqueous solution of calcium bicarbonate containing a gelatinising organic colloid.

#### EXPERIMENTAL.

The solution of calcium bicarbonate was prepared by passing carbon dioxide into a saturated solution of lime water. In this way a stock solution could be prepared at room temperature containing 0.0134 g.-mol. of calcium carbonate per litre.

With organic colloids such as gum arabic, gum tragacanth, and fish glue, no iridescent structures could be obtained by the method employed in these experiments. The best results were obtained with commercial leaf gelatin (containing 10% of moisture and 1.924% of ash). Iridescent deposits could not be obtained with a sample of highly purified and almost ash-free gelatin prepared in this laboratory. Liesegang (*Z. physikal. Chem.*, 1914, **88**, 1) has found that the best rings of silver chromate are produced when the gelatin contains small quantities of "gelatose" (a hydrolytic product of gelatin) as well as acid. All samples of commercial gelatin contain "gelatose" and therefore are most suitable for the production of Liesegang periodic layers.

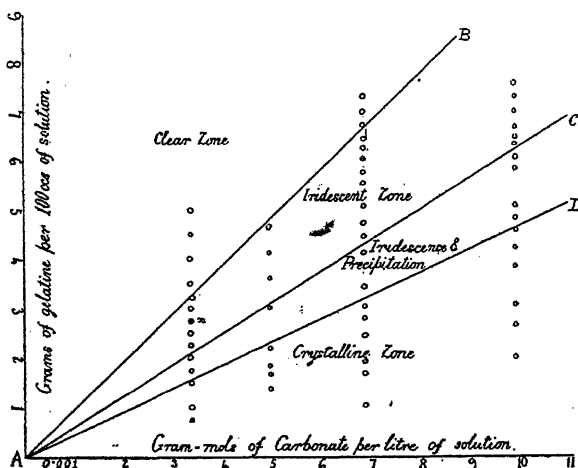
The method of procedure was as follows. Varying amounts of gelatin were weighed into a series of test-tubes, to which measured volumes of water were added. The tubes were then stoppered and the gelatin was allowed to swell, after which it was dissolved by immersing the tubes in hot water. When the solutions had cooled to about 40°, measured volumes of the calcium bicarbonate solution were run in, the contents of each tube thoroughly mixed, and drops from each placed on clean glass plates. The thin layers of gelatin-bicarbonate solution thus produced were allowed to evaporate slowly at room temperature. More rapid evaporation either at higher temperatures (*e.g.*, 50°) or in desiccators containing drying agents (or alkalis to absorb carbon dioxide) failed to give iridescent deposits of calcium carbonate. Another factor of importance in the

production of iridescence is the initial thickness of the layer of solution on the glass plate. The best results are obtained when this thickness lies between 1 and 3 mm.

An examination of the dried layers showed that for a given initial concentration of calcium carbonate the result depended on the concentration of gelatin. With any given initial calcium carbonate concentration and increasing gelatin concentrations, four types of product, corresponding to four fairly well demarcated regions, were in general obtained :

*Region 1.*—If the gelatin concentration lies below a certain value, there is produced an irregular crystalline deposit, with a thicker aggregation of calcium carbonate crystals at the centre, but no iridescence.

FIG. 1.



*Region 2.*—If the gelatin concentration is somewhat higher, iridescent specks appear, generally in the centre, together with a visible deposit of calcium carbonate crystals all over the area. In this case the calcium carbonate usually formed a series of coarse irregular rings.

*Region 3.*—With a still higher gelatin concentration there is no visible deposit of calcium carbonate, and the whole area, now quite translucent, shows a beautiful mother-of-pearl-like iridescent colour, varying with the angle of observation.

*Region 4.*—Finally, if the gelatin concentration exceeds a certain value, the layer remains clear and translucent, but exhibits no colour.

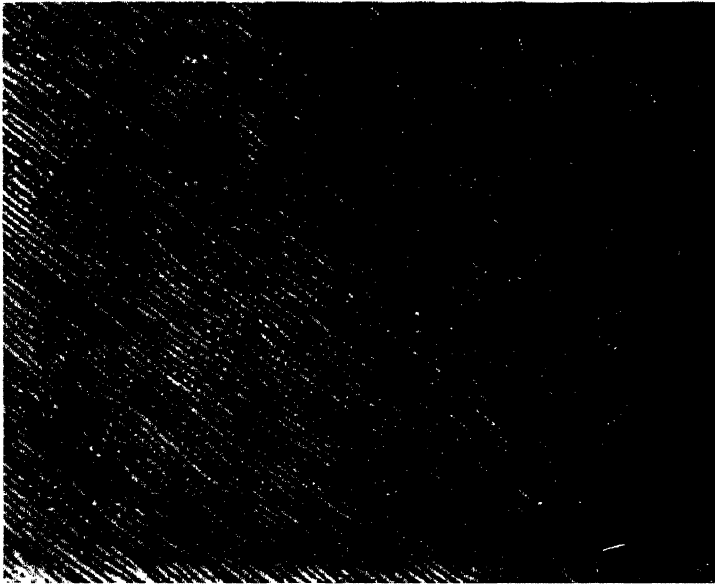
The general nature of the results obtained is well shown in the accompanying figure. The lines AB, AC, AD, together with the axes, divide the diagram into the four regions or zones already

described, although it must be understood that the positions of these lines are not fixed with any great degree of precision.

Microscopic examination of the thin iridescent plates of gelatin-calcium carbonate corresponding to the zone AB—AC shows that the slowly decomposing calcium bicarbonate has deposited the calcium carbonate in a series of more or less regular and parallel layers or sheets resembling those of a Liesegang structure. Various photomicrographs were taken and the spacing of the layers was determined by means of a Hilger travelling microscope. There were present 4000—6000 layers per cm. The accompanying photograph shows the type of structure obtained.

#### *Discussion of Results.*

These experiments show that it is possible to prepare a clear, translucent, thin plate or sheet of dried gelatin containing a very fine spatially periodic precipitation of calcium carbonate and exhibiting the iridescent colour effects characteristic of mother-of-pearl. The colours shown by the preparations described in this paper are in all probability due to a grating effect caused by the closely-spaced layers of calcium carbonate, although it has not been found possible to determine by means of sections the exact orientation of these layers with respect to the surface of the thin plate of gelatin. Nevertheless, the photomicrographs show clearly enough that the layers of calcium carbonate do not lie parallel to the surface of the gelatin plane, but must be oriented at an angle to it which probably does not differ much from  $90^\circ$ . Each drop of solution produces a thin, more or less circular, lens-shaped disc on the glass plate. It is probable that the precipitation of calcium carbonate begins at the surface of the outer rim, and proceeds rhythmically in a series of closely-spaced concentric rings towards the central part of the surface of the evaporating disc of solution. As evaporation of water and carbon dioxide proceeds, this rhythmic precipitation is carried more or less vertically downwards, *i.e.*, at right angles to the main surface of the disc. The result of such a periodic precipitation would be to yield a grating surface capable of producing colours in reflected light, provided the spacing be fine enough. Although this is the most probable explanation of the colour effects described in this paper, the possibility of colour production by interference of light reflected from a series of parallel plates cannot be excluded. Taken in conjunction with the work of Brewster and of Lord Rayleigh, the synthetic chemical experiments described leave little doubt as to the origin of the colours exhibited by mother-of-pearl. The thin sheets of gelatin-calcium carbonate which have been obtained approach very closely in their nature and structure



*Microphotograph of gelatin-calcium carbonate. ×560.  
(Corresponding to x in the figure.)*

*[To face p. 188i.]*



to natural mother-of-pearl, and may indeed be described as "elements" of mother-of-pearl, although, of course, the organic colloid used is different from the "conchiolin" of the natural material.

*Summary.*

1. The deposition of calcium carbonate from a thin layer of an aqueous solution of calcium bicarbonate in the presence of gelatin has been studied.

2. The nature of the deposit depends upon the initial concentration of calcium bicarbonate and the ratio of gelatin to calcium bicarbonate.

3. For any given initial concentration of calcium bicarbonate there is a range of gelatin concentrations which yield translucent layers showing the iridescent colours characteristic of mother-of-pearl.

4. The structure of mother-of-pearl has been discussed in the light of these experiments and the physical work of Brewster and of Lord Rayleigh.

In conclusion, the author wishes to express his thanks to Professor Donnan for suggesting this problem to him and for his kind interest and guidance in the work.

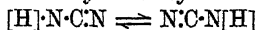
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PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE,  
LONDON.

[Received, March 16th, 1926.]

CLXXIX.—*Aminobenzthiazoles. Part III. The Tautomerism and Unsaturation of the Aminothiazole System.*

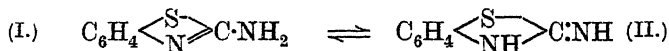
By ROBERT FERGUS HUNTER.

As one of the three objects\* of this investigation (see Part I, J., 1925, 127, 2023), the mobility of the symmetrical triad system



\* A fourth object, viz., the study of the relation between unsaturation and mobility in tautomeric triad systems of the aminothiazole type, is of particular interest in connexion with the whole philosophical aspect of tautomerism involving a mobile hydrogen atom (compare Thorpe, J., 1923, 123, 1361; Kon, Stevenson, and Thorpe, J., 1922, 121, 650), and will be fully dealt with in a later paper. In the 5-bromo-1-alkylaminobenzthiazoles, the increasing molecular volume of the alkyl group in the ethyl, *n*-propyl, *n*-butyl, *isobutyl* series tends to enhance the aminothiazole phase of the system, and consequently to increase the stability of the dibromo-addition compounds. Indeed, in the ethyl series Mr. Soyka and myself were able

in 1-amino- and substituted 1-aminobenzthiazoles has been examined, with the result that the tautomerism of the 1-aminobenzthiazole system (I) with the corresponding 1-imino-1:2-dihydrobenzthiazole complex (II) has been established.



There are three tests for the mobility of symmetrical triad systems (Ingold and Piggott, J., 1922, **121**, 2381; 1923, **123**, 1470): (A) The symmetry test, (B) the fission test, and (C) the substitution test (compare also Farrow and Ingold, J., 1924, **125**, 2543). Only the first and third of these tests are applicable to the system under discussion. There exists already in the literature of 1-aminobenzthiazole evidence of the symmetry type. Thus, whilst the classical synthesis of this compound from 1-chlorobenzthiazole (Hofmann, *Ber.*, 1879, **12**, 1126) is usually regarded as a proof of the constitution (I), its synthesis from phenylthiosemicarbazide (Fischer and Besthorn, *Annalen*, 1882, **212**, 326) \* can be formulated only in terms of the iminodihydro-structure (II).

The symmetry test, however, was more definitely established by the synthesis of 1-acetylaminobenzthiazole (VII) and 1-imino-2-acetyl-1:2-dihydrobenzthiazole (VIII) from the bromides (V) and (VI), respectively, which were obtained by bromination of the stable and labile forms of acetylphenylthiocarbamide (Hugershoff, *Ber.*, 1899, **32**, 3649; Wheeler, *Amer. Chem. J.*, 1902, **27**, 270; Hunter, *loc. cit.*). On hydrolysis, the two isomeric acetyl derivatives

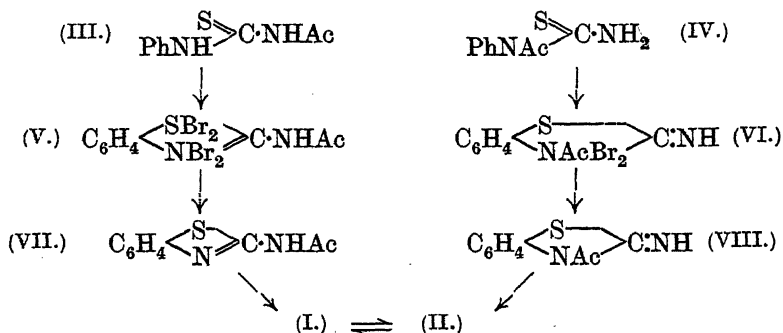
to isolate both forms of the dibromide, which must be regarded as being of the type  $[H]NBr_2 \cdot C \cdot N \cdot Et$  and  $NBr_2 \cdot C \cdot N[H]Et$ , respectively. These forms were strikingly different in physical properties and in their reducibility by hydriodic acid (compare West, J., 1924, **125**, 710 and other papers). Both gave the same ethylamino-base on reduction with sulphurous acid and, moreover, the labile form was converted into the more stable form by boiling for some time with a mixture of bromine and chloroform. This conversion shows that it is at least probable that at some stage an equilibrium  $[H]NBr_2 \cdot C \cdot N \cdot Et \rightleftharpoons NBr_2 \cdot C \cdot N[H]Et$ , which is apparently a case of retarded mobility (Kon and Linstead, J., 1925, **127**, 815) involving quinquevalent nitrogen, may occur. In view of this, it has seemed desirable to institute a series of experiments on the bromination both of mobile and of "nascently" mobile (compare Goss and Ingold, J., 1925, **127**, 2776) systems of the amidine type.

In the bromination of *s*-di- $\beta$ -naphthylthiocarbamide in chloroform (J., 1925, **127**, 2270) two forms of the hexabromide of 2- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole were accidentally isolated, and only one of these was obtained by bromination of the naphthathiazole base itself.

\* Fischer and Besthorn's "phenylthiocarbazine," obtained by the action of 20% hydrochloric acid on phenylthiosemicarbazide at 125–130°, was shown by Hugershoff (*Ber.*, 1903, **36**, 3134) to be 1-aminobenzthiazole.



(VII and VIII) yielded the same 1-aminobenzthiazole (or 1-imino-1:2-dihydrobenzthiazole).



With regard to the third test (C), it was found that 1-aminobenzthiazole methylates almost exclusively in the imino-form (II), yielding 1-imino-2-methyl-1:2-dihydrobenzthiazole (XI), whose constitution was established by rational synthesis from *as*-methylphenylthiocarbamide (IX) by way of the *dibromide* (X). During the methylation a more soluble isomeride was also produced. This, owing to experimental difficulties, could not be obtained pure, but it was undoubtedly 1-methylaminobenzthiazole (XIV), which was also synthesised from *s*-methylphenylthiocarbamide (XII) by way of the *tetrabromide* (XIII). [Formulae IX, X, and XI are IV, VI, and VIII, respectively, and XII, XIII, and XIV are III, V, and VII, respectively, all with Me in place of Ac.]

The ethylation of 1-aminobenzthiazole proved more troublesome than the methylation. The bulk of the product was, however, finally identified as 1-imino-2-ethyl-1:2-dihydrobenzthiazole, whose constitution was established by its synthesis from *as*-ethylphenylthiocarbamide by way of the *tetrabromo*-addition compound as in the case of the corresponding methyl derivative.

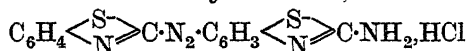
The acetylation of 1-aminobenzthiazole was studied in the hope of isolating both acetyl derivatives (VII and VIII). The base acetylated almost completely in the amino-form (I), giving 1-acetylaminobenzthiazole, and although on several occasions the presence of a small amount of a low-melting acetyl derivative was observed, the second isomeride could not be isolated pure.

The substitution test (C), therefore, supports the symmetry test (A), since with a reagent favouring the imino-form, the triad system reacts almost completely in this form, the methyl group attaching itself almost exclusively to the less basic nitrogen atom (Marckwald, *Annalen*, 1895, **286**, 343; von Pechmann, *Ber.*, 1895, **28**, 869, 2362; 1897, **30**, 1779; Cohen and Marshall, *J.*, 1910, **97**, 328), whilst with

acetic anhydride, which favours the amino-form, the amidine system reacts almost completely in the latter form, yielding the 1-acetyl-amino-derivative.

Although experimental difficulties prevented the isolation in a pure condition of two methyl or ethyl derivatives, there can be no doubt that in both cases both alkyl derivatives were actually present, for Pyman has shown (J., 1923, 121, 367, 3359) that, on alkylation, an amidine whose two nitrogen atoms differ in basicity invariably yields two alkyl derivatives, a very small quantity of the isomeride corresponding to the more basic form of the amidine accompanying a large quantity of the more readily formed alkyl derivative. The two nitrogen atoms in the aminothiazole system differ considerably in basicity, this being shown by the base acetylating almost completely in the more basic form.

Mobility in 1-aminobenzthiazole having thus been established, the general chemistry of the substance was studied. The base was readily converted into an unstable diazonium chloride, which coupled with  $\beta$ -naphthol in the usual way. Attempts to convert the diazonium chloride into 1-hydroxybenzthiazole, however, invariably yielded 1-aminoazobenzthiazole hydrochloride,



(compare Hantzsch and Popp, *Annalen*, 1889, 250, 257).

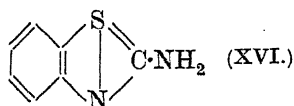
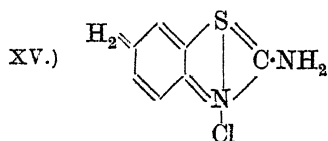
The aminothiazole appeared to react in the normal way with formaldehyde and acetaldehyde, but pure condensation products could not be isolated. Attempts to condense the base with benzaldehyde failed. This is readily understood, however, since the formation of the benzyldene derivative would involve the removal of both the mobile hydrogen atom and the potentially mobile hydrogen atom of the triad system.

The base benzoylated normally, giving 1-benzoylamino benzthiazole, which on treatment with an excess of bromine yielded a tetrabromide (formula as V). Under the influence of dilute alcohol this yielded 5-bromo-1-benzoylamino benzthiazole. The fact that the presence of a benzoyl group only allows the formation of a tetrabromide in circumstances in which 1-acetylamino benzthiazole readily passes into a hexabromide is probably to be attributed to the steric effect of the phenyl group in the benzoylamino-residue.

1-Aminobenzthiazole reacts very readily with sodium hypochlorite, yielding a deep purple dye of the rosaniline type.

On treating 1-aminobenzthiazole hydrochloride with alcoholic ethyl nitrite, neither the expected 1-imino-2-nitroso-1:2-dihydrobenzthiazole nor benzthiazole itself was produced, but the hydrochloride of a new base, isomeric with 1-aminobenzthiazole, which

crystallised in beautiful ruby-red prisms. The base itself was very pale yellow. A similar reaction was observed in the cases of 1-amino-3-methyl- and 1-amino-5-methyl-benzthiazole. Possibly the intensely coloured hydrochloride and the base may have formulæ (XV) and (XVI), respectively (compare Kehrman, *Ber.*, 1906, **39**, 914; Smiles and Hilditch, *J.*, 1908, **93**, 145, 1687; Battegay and Vechot, *Bull. Soc. chim.*, 1925, **37**, 1271).

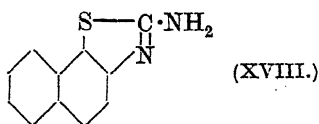
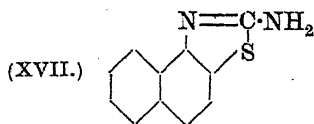


The tautomerism of 5-bromo-1-aminobenzthiazole and 5-bromo-1-imino-1:2-dihydrobenzthiazole was established by means of the symmetry test (A). The hexabromide of 1-acetylaminobenzthiazole,  $C_6H_4 \begin{smallmatrix} SBr_4 \\ NBr_2 \end{smallmatrix} > C \cdot NHAc$ , was converted into 5-bromo-1-acetylaminobenzthiazole, and the dibromide of 1-imino-2-acetyl-1:2-dihydrobenzthiazole (VI) into the isomeric 5-bromo-1-imino-2-acetyl-1:2-dihydrobenzthiazole, by treatment with dilute alcohol (compare Hunter, *J.*, 1925, **127**, 2026). On hydrolysis both these 5-bromo-acetyl derivatives yielded the same 5-bromo-1-aminobenzthiazole (formula as I or II). The fission test (B) is inapplicable in this case, and the substitution test (C) was not investigated in view of the difficulties encountered in the previous case.

In view of the curious observations made regarding the bromides of the *o*-, *m*-, and *p*-toluidinomethylbenzthiazoles (*loc. cit.*), the bromo-addition compounds of 1-amino-3-methyl-, 1-amino-4-methyl- and 1-amino-5-methyl-benzthiazole were examined. Whereas *o*-tolylthiocarbamide readily passed into the dibromide of the first, *m*-tolylthiocarbamide gave the labile tetrabromide of the second,  $C_6H_3Me \begin{smallmatrix} SBr_2 \\ NBr_2 \end{smallmatrix} > C \cdot NH_2$ , whilst *p*-tolylthiocarbamide yielded a more stable tribromo-addition compound of the last, which is doubtless the hydrobromide of the dibromide. This tribromide was on one occasion isolated in two forms (compare the case of 2-β-naphthylamino-α-naphthathiazole hexabromide, *J.*, 1925, **127**, 2274).

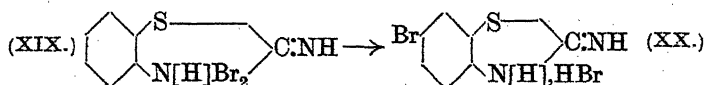
Bromination of *m*-xylylthiocarbamide gave the tetrabromide of 1-amino-3:5-dimethylbenzthiazole, which is the most labile aminothiazole bromide so far isolated. The instability is clearly to be attributed to the methyl groups in positions 3 and 5, there being no possibility either of *o*- or of *p*-migration of bromine into the aromatic nucleus (compare Fries, *Annalen*, 1906, **346**, 128).

Lastly, the bromides of 2-amino- $\beta$ -naphththiazole (XVII) and 2-amino- $\alpha$ -naphththiazole (XVIII) were examined. Both  $\alpha$ - and  $\beta$ -naphthylthiocarbamide on bromination readily yielded the *tetrabromides* of (XVII) and (XVIII), respectively. These are compounds of the usual type, but are more stable than the bromides of the aminobenzthiazole series, no doubt owing to the presence of the naphthalene nucleus, since the bromo-addition compounds of 2- $\beta$ -naphthylamino- $\alpha$ -naphththiazole (*loc. cit.*) are remarkably stable under ordinary laboratory conditions.



1-Imino-2-methyl-1 : 2-dihydrobenzthiazole (XI) on bromination yielded a stable orange-yellow *tribromide* of the type obtained by exposing the higher bromides of the 1-tolylaminodimethylbenzthiazole series (*loc. cit.*) to moist air.

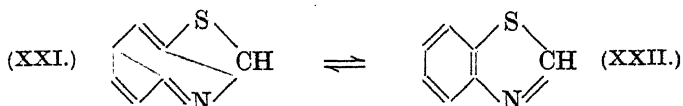
The dibromide of 1-aminobenzthiazole (XIX) (Hugershoff, *Ber.*, 1901, **34**, 3130; 1903, **36**, 3121) obtained by brominating phenylthiocarbamide in chloroform, on treatment with warm water, is instantly converted into 5-bromo-1-imino-1 : 2-dihydrobenzthiazole hydrobromide (XX).



This transformation is clearly a *para*-migration, analogous in some respects to the *N*-bromoacetanilide  $\rightarrow$  *p*-bromoacetanilide isomerisation (Chattaway and Orton, *J.*, 1899, **75**, 1046; 1900, **77**, 134, 152, 789, 797), but differing from it in that the nitrogen atom is in the quinquivalent state. The passage of the dibromide into the bromo-hydrobromide can be explained by means of a bridged form of the benzthiazole nucleus (XXI) (compare Ingold, *J.*, 1922, **121**, 1133, 1143) analogous to the formula which Shearer (*Proc. Phys. Soc.*, 1923, **35**, ii, 81) has assigned to naphthalene on the basis of *X*-ray analysis.\*

\* The parachors (*J.*, 1925, **127**, 1525 and later papers) of 1-aminobenzthiazole and of certain other benzthiazole derivatives are being determined by Dr. Sugden in the hope that they may give some indication of the intramolecular exchanges which take place in the benzthiazole system. Unfortunately, the difference between the calculated values of the parachor for the ordinary form of 1-aminobenzthiazole (I or II) ( $[P] = 311.9$ ) and for the bridged form suggested in this paper as a phase of the benzthiazole system ( $[P] = 308.9$ ) is very small (Sugden, private communication) and may not be capable of definite experimental detection.

The bridged formula (XXI) represents only *one* of the intra-annular phases of benzthiazole, in tautomeric equilibrium with the



normal phase (XXII), which is the usually accepted structure for the substance. The bridged form involves a hypothetical form of the thiazole nucleus, analogous to the bridged formula of thiophen (Farmer, Ingold, and Thorpe, J., 1922, **121**, 134) and the intra-annular five-carbon nucleus (*idem*, *loc. cit.*; Ingold, Seeley, and Thorpe, J., 1923, **123**, 863; Grimwood, Ingold, and Thorpe, *ibid.*, p. 3303). The strikingly aromatic properties of the thiazole nucleus (Hantzsch and collaborators, *loc. cit.*) suggest that the thiazole ring must, if the views of Ingold and his collaborators (J., 1922, **121**, 1133, 1143; 1923, **123**, 2066, 2081) regarding aromatic nuclei are correct, be a tautomeric system, although in view of the difficulties which heterocyclic nuclei present in this connexion from the experimental point of view (Ingold and Piggott, J., 1922, **121**, 2749; Ingold, J., 1924, **125**, 87), the problem of obtaining direct evidence of a bridged form of the thiazole nucleus appears at the present time to be insoluble. Evidence of a bridged form of the benzthiazole system must, however, be taken as *indirect* evidence on this point, and a series of experiments has been instituted in the hope of proving that the bridged formula (XXI) represents *one* phase of the benzthiazole system. With regard to the 1-amino-benzthiazole dibromide  $\rightarrow$  5-bromo-1-imino-1:2-dihydrobenzthiazole hydrobromide change, it is suggested, not that this transformation is a proof of the bridged structure of the benzthiazole nucleus, but merely that it is best explained on the basis of the latter. The exceedingly beautiful fluorescence of certain benzthiazole derivatives (Hunter, *Chemical News*, 1923, **127**, 385) is noteworthy in connexion with the problem of the bridged phase (compare Kaufmann, *Ahrens Vorträge*, 1908, **12**, 35; Ingold, J., 1922, **121**, 1134).

#### EXPERIMENTAL.

(Substances exhibiting amino-iminodihydro-tautomerism are named on the basis of their amino-formula).

##### *The Mobility of 1-Aminobenzthiazole.*

*Methylation.*—1-Aminobenzthiazole (2 g.) was heated with methyl iodide (1.6 c.c.) at 100° for 5 hours. The product, after being treated with alkali and with hot water to remove any unchanged amino-base, crystallised from alcohol in plates, m. p. 115°. After

recrystallisation from benzene it melted at  $122^{\circ}$  and did not depress the m. p. of an authentic specimen of 1-imino-2-methyl-1:2-dihydrobenzthiazole (XI). It was further characterised by the formation of the stable, yellow-orange tribromo-addition compound (page 1393).

In an experiment similar to the above, the methylation product was extracted with cold ether and alcohol. The extract on evaporation yielded a clear pale yellow gum, which could not be crystallised, consisting of the more soluble methyl derivative. After the gum had solidified, it melted at about  $114^{\circ}$ . Mixed with a specimen of 1-methylaminobenzthiazole, it melted at  $120^{\circ}$  after softening at about  $100^{\circ}$ .

*Ethylation.*—1-Aminobenzthiazole (2 g.) and ethyl iodide (1.5 c.c.) were heated at  $100^{\circ}$  for 5–6 hours. The product, after treatment with alkali and warm water, was usually obtained as a tenacious gum, which sometimes solidified on standing for some weeks. On trituration with ether the product sometimes crystallised. It had m. p.  $85^{\circ}$  and was identified as 1-imino-2-ethyl-1:2-dihydrobenzthiazole (mixed melting point determination).

*Acetylation.*—A solution of 8 g. of 1-aminobenzthiazole in acetic anhydride (30 c.c.) was heated under reflux and cooled and the crystalline acetyl derivative was collected. The filtrate was mixed with alcohol and evaporated; small needles, m. p.  $115^{\circ}$ , were thus obtained. The acetyl derivative (7 g.) was extracted with boiling alcohol; the residue of small prisms had the same m. p.,  $186^{\circ}$ , as the lustrous plates of 1-acetylaminobenzthiazole deposited from the extract. The remaining liquors were fractionally crystallised, but although low-melting substances (m. p.  $120^{\circ}$ ) were frequently obtained, 1-imino-2-acetyl-1:2-dihydrobenzthiazole could not be isolated pure. The yield of pure 1-acetylaminobenzthiazole was almost quantitative. The crude acetylation product had no action on sodium hypobromite, showing the absence of unchanged base.

*1-Imino-2-methyl-1:2-dihydrobenzthiazole Dibromide (X).*—*as-Methylphenylthiocarbamide* (1 g.) in chloroform (10 c.c.) was gradually treated with a solution of bromine (0.8 c.c.) in chloroform (3 c.c.); a bulky orange precipitate separated which redissolved with evolution of heat and hydrogen bromide. The mixture was refluxed for 2 minutes and cooled; the bulk of the product then separated in tile-red crystals. The filtrate gradually deposited the *dibromide* in glistening, orange-red needles which, after drying in a vacuum over potassium hydroxide, sintered and softened at  $125^{\circ}$  (Found: Br, 49.8.  $C_8H_8N_2Br_2S$  requires Br, 49.4%). The *dibromide* had the usual properties of these compounds, and slowly became yellow in the air with loss of bromine.

1-*Imino-2-methyl-1 : 2-dihydrobenzthiazole* (XI).—The dibromide, suspended in sulphurous acid, was treated with sulphur dioxide until a colourless solution was obtained. This, on being made alkaline with ammonia, deposited the free methyl base in small prisms, m. p. 123° (Found : S, 18.9.  $C_8H_8N_2S$  requires S, 19.5%).

1-*Imino-2-methyl-1 : 2-dihydrobenzthiazole Tribromide*.—The methyl derivative (0.2 g.) dissolved in chloroform (7 c.c.) was slowly treated with an excess of a 20% solution of bromine in the same solvent; an orange precipitate of the bromo-addition compound was obtained. The mixture was warmed and then cooled in ice. The *tribromide*, after being dried in a vacuum, was obtained in minute, orange prisms which lightened at 230–240° and became white without melting at 245° [Found : Br, 59.8.  $(C_8H_8N_2Br_3S)_2$  requires Br, 59.4%].

1-*Methylaminobenzthiazole Tetrabromide* (XIII).—A solution of *s*-methylphenylthiocarbamide (4 g.) in chloroform (25 c.c.) was gradually treated with bromine (3.2 c.c.) and heated under reflux for a few minutes. On cooling, the *tetrabromide* crystallised in rosettes of shining, scarlet needles, m. p. 65–67° (decomp.), which were dried in a vacuum over potassium hydroxide (Found : Br, 66.1.  $C_8H_8N_2Br_4S$  requires Br, 66.1%).

The tetrabromide was exposed to the air for 20 hours (compare 1-anilinobenzthiazole tetrabromide → tribromide transformation; J., 1925, 127, 2026), losing bromine with the formation of a yellow-orange *dibromide*. This was extracted with chloroform, and separated on scratching in small, orange-yellow prisms which, after drying in a vacuum, sintered at 136° and charred at 191° (Found : Br, 48.8.  $C_8H_8N_2Br_2S$  requires Br, 49.4%). The dibromide, however, differed from the tribromides of the 1-arylaminobenzthiazoles (*loc. cit.*) in losing more bromine on prolonged exposure to air.

*Bromo-substitution Derivatives*.—The tetrabromide dissolved readily in hot absolute alcohol, and on diluting the solution with water and concentrating it, a crystalline mass of the hydrobromides of the bromo-substitution products was obtained. This was treated with ammonia and the liberated bases were crystallised from ethyl acetate-alcohol, from which silky, lustrous plates of a mixture of monobromo- and dibromo-substitution derivatives were obtained, m. p. 203°; these could not be separated (Found : Br, 46.8.  $C_8H_7N_2BrS$  requires Br, 37.0%.  $C_8H_6N_2Br_2S$  requires Br, 49.9%). This behaviour is curious, for in all previous experiments on the bromination of substituted benzthiazoles it was possible to introduce only one bromine atom into the benzene nucleus (Hunter, this vol., p. 540).

1-*Methylaminobenzthiazole* (XIV).—The tetrabromide was suspended in sulphurous acid and treated with sulphur dioxide. The crystalline paste of salts obtained was slowly added to a strong solution of ammonia, in which it dissolved. The base crystallised on cooling, and a further small quantity was obtained by extracting the filtrate with ether. The base was obtained from dilute alcohol in tufts of silky needles, m. p. 135°, and finally from absolute alcohol in prisms, m. p. 138° (Found: S, 19.8.  $C_8H_8N_2S$  requires S, 19.5%).

1-*Imino-2-ethyl-1 : 2-dihydrobenzthiazole tetrabromide* was obtained from *as*-ethylphenylthiocarbamide (3 g.) and bromine (2.2 c.c.) in chloroform by the method for preparing the dibromide (X). After drying in a vacuum over potassium hydroxide, the tetrabromide was obtained in glistening, vermilion-orange prisms, m. p. 160—161° (decomp., with previous sintering) (Found: Br, 62.6.  $C_9H_{10}N_2Br_4S$  requires Br, 64.3%).

1-*Imino-2-ethyl-1 : 2-dihydrobenzthiazole*, prepared by reducing the preceding tetrabromide (10 g.) in the usual way, was obtained as a gum which solidified; it crystallised from alcohol in pale yellow prisms, m. p. 86° (Found: S, 18.1.  $C_9H_{10}N_2S$  requires S, 17.9%).

*Labile Acetylphenylthiocarbamide*.—Phenylthiocarbamide (16 g.) was heated with acetic anhydride (14 c.c.) at 80° (Hugershoff, *loc. cit.*). The product crystallised from ethyl acetate in prisms, m. p. 136°; after recrystallisation it melted at 138°.

1-*Imino-2-acetyl-1 : 2-dihydrobenzthiazole Dibromide* (VI).—(A) The labile acetylphenylthiocarbamide (2 g.) dissolved in chloroform (25 c.c.) was gradually treated with bromine (1.2 c.c.). Heat and hydrogen bromide were evolved in the usual way and crystallisation took place in the hot solution towards the end of the bromination. The mixture was refluxed for a short time, cooled, and the *dibromide* collected and dried in a vacuum; it was then obtained in glistening orange prisms, m. p. 130—132° (decomp.) (Found: Br, 45.6.  $C_9H_8ON_2Br_2S$  requires Br, 45.5%).

(B) The acetylphenylthiocarbamide (2 g.) dissolved in 12 c.c. of chloroform was gradually treated with 1.6 c.c. of bromine; hydrogen bromide was evolved and a dark red tar produced. The solvent was decanted off and the tar boiled for 1 minute with 20 c.c. of absolute alcohol, being thereby changed into fine purplish-red prisms, which were dried in a vacuum. This *dibromide* sintered at about 160° and melted at 173° (decomp.) (Found: Br, 42.3%).

This dibromide showed the most striking stability to air, and appreciably lost bromine only over a period of some weeks. It was also more slowly reduced by sulphurous acid than the other bromides of 1-imino-2-acetyl-1 : 2-dihydrobenzthiazole.



*1-Imino-2-acetyl-1 : 2-dihydrobenzthiazole Dibromide Hydrobromide.*—The labile acetylphenylthiocarbamide (4 g.) dissolved in chloroform (30 c.c.) was gradually treated with bromine (3 c.c.), and the mixture boiled. The product consisted of small, shining, dark chocolate-coloured prisms which were dried in the usual way. They became suddenly orange at 178° and melted at 180° (decomp.) (Found: Br, 55.6.  $C_9H_8ON_2Br_2S \cdot HBr$  requires Br, 55.7%). This bromide had the usual properties, being reduced by sulphurous acid and converted into the substitution derivative by treatment with diluted alcohol, and was strikingly similar to the dibromide of 4'-amino-1-phenyl-5-methylbenzthiazole (J., 1925, 127, 1318) in appearance and stability in air.

*1-Imino-2-acetyl-1 : 2-dihydrobenzthiazole (VIII).*—This was obtained from the dibromide by means of sulphurous acid and ammonia in the usual way. It separated from 20% alcohol in minute crystals, m. p. 118—120° (Found: S, 17.2.  $C_9H_8ON_2S$  requires S, 16.7%).

*Hydrolysis.* A part of the product was hydrolysed with 60% sulphuric acid, the solution neutralised at 0°, and the product recrystallised from hot water. Lustrous plates of 1-aminobenzthiazole were thus obtained which, alone or mixed with a genuine specimen, melted at 126°. The base was further characterised by the formation of the dibromide and of benzthiazole-1-azo- $\beta$ -naphthol.

Specimens of the acetyl derivative have sometimes been obtained from alcohol-ethyl acetate in pale yellow prisms, m. p. 140° (or higher); these also yield 1-aminobenzthiazole on hydrolysis with 60% sulphuric acid, but have not yet been fully investigated.

*Stable Acetylphenylthiocarbamide.*—The labile acetyl derivative (18 g.) was kept at 150—160° for 10 minutes and then at 170—180° for an equal time. The product crystallised from alcohol-ethyl acetate in prisms, m. p. 170—171°, as recorded (*loc. cit.*).

*1-Acetylaminobenzthiazole Tetrabromide (V).*—When stable acetylphenylthiocarbamide (1 g.) in chloroform (7 c.c.) was slowly treated with bromine (0.9 c.c.), hydrogen bromide was evolved and a clear red gum separated. The mixture was boiled and cooled. On being rubbed, the gum solidified to a mass of orange-red prisms which were dried in the usual way; m. p. 137—139° (Found: Br, 61.8.  $C_9H_8ON_2Br_4S$  requires Br, 62.5%).

*1-Acetylaminobenzthiazole (VII)* was obtained from the tetrabromide (1 g.) in the usual way. It crystallised from alcohol in prisms, m. p. 186°, and was identical with the acetyl derivative obtained by the direct acetylation of 1-aminobenzthiazole.

*1-Benzoylaminobenzthiazole*, obtained from 1-aminobenzthiazole

(1 g.) by the Schotten-Baumann method, crystallised from alcohol in prisms, m. p.  $186^{\circ}$  (Hugershoff, *loc. cit.*).

*1-Benzoylamino benzthiazole Tetrabromide*.—The benzoyl derivative (0.4 g.) dissolved in 5 c.c. of chloroform was treated with bromine (0.3 c.c.), and the solution boiled. On cooling, the *tetrabromide* crystallised in silky, orange-yellow plates which, after drying in a vacuum, lightened in colour at about  $170^{\circ}$  and became colourless and lost bromine at about  $185^{\circ}$  (Found: Br, 56.8.  $C_{14}H_{10}ON_2Br_4S$  requires Br, 55.8%).

*5-Bromo-1-benzoylamino benzthiazole*.—A solution of the tetrabromide in alcohol was boiled, diluted, and evaporated, the white, crystalline product was treated with ammonia, and the *bromo-derivative* was dried and recrystallised from ethyl acetate, separating in small prisms, m. p.  $226^{\circ}$  (Found: Br, 25.2.  $C_{14}H_9ON_2BrS$  requires Br, 24.0%).

*Benzthiazole-1-azo- $\beta$ -naphthol*.—A solution of aminobenzthiazole (1.5 g.) in 20 c.c. of dilute hydrochloric acid was diazotised in the usual way, and the product coupled with 1.4 g. of  $\beta$ -naphthol dissolved in 8 c.c. of 5% sodium hydroxide solution. The orange-brown azo-compound was collected and extracted with ether; the extract, on evaporation in a vacuum at room temperature, left the azo-compound in deep purple-red prisms, m. p.  $146^{\circ}$  after sintering at  $140^{\circ}$  (Found: S, 10.3.  $C_{17}H_{11}ON_3S$  requires S, 10.5%). The product dyed cotton a fugitive shade of yellow. On reduction with tin and hydrochloric acid it gave 1-aminobenzthiazole, which was identified by its m. p. and by the m. p. of its mixture with a genuine specimen.

*1-Aminoazobenzthiazole*.—A solution of diazotised 1-aminobenzthiazole (prepared from 4 g. of the base in 50 c.c. of water and 10 c.c. of concentrated hydrochloric acid) was boiled for an hour, filtered from tar [which did not yield any trace of 1-hydroxybenzthiazole (Jacobson, *Ber.*, 1886, 19, 1811) on extraction with alkali] and concentrated. The red crystals of the *hydrochloride* obtained separated from alcohol (animal charcoal) in yellow prisms, m. p.  $232^{\circ}$  (decomp.) after softening at  $224^{\circ}$ . The *base* was obtained by treating it with ammonia and was crystallised from ether and from boiling water, separating in small, cream-white, lustrous plates, m. p.  $135^{\circ}$  (Found: S, 21.6.  $C_{14}H_9N_5S_2$  requires S, 20.7%). On reduction with tin and hydrochloric acid, 1-aminobenzthiazole was isolated and identified (m. p. and mixed m. p. determination).

*Reaction of 1-Aminobenzthiazole with Sodium Hypochlorite*.—The base (1 g.) in 30 c.c. of water was gradually treated with 50 c.c. of 0.3*N*-sodium hypochlorite. The purple precipitate produced, after being washed with a little ether, separated from chloroform—

light petroleum at 20° in dark purple crystals, which softened at 156—158°. The compound had dyeing properties of the usual type.

*ψ-Aminobenzthiazole Hydrochloride (XV).*—The hydrochloride from 5 g. of 1-aminobenzthiazole was suspended in 80 c.c. of alcohol at 5° and slowly treated with 16.5 c.c. of a 15% alcoholic solution of ethyl nitrite. The mixture became yellow on addition to 50 c.c. of boiling alcohol and thereafter bright orange on refluxing for a short time. On spontaneous evaporation, clusters of hard, shining, ruby-red prisms were obtained, which were washed with ether and recrystallised from alcohol. The *hydrochloride* was thus obtained in deep orange needles, m. p. 239—240° (Found: Cl, 19.6.  $C_7H_6N_2S \cdot HCl$  requires Cl, 19.1%).

*ψ-Aminobenzthiazole (XVI).*—The bright yellow base obtained by treating the red hydrochloride with ammonia (*d* 0.880) was dried and recrystallised from "sodium-dried" benzene at 20°, separating in slender, pale yellow needles which sintered and softened at 129° and melted to a clear purple-red liquid at 131° (Found: N, 18.4; S, 21.6.  $C_7H_6N_2S$  requires N, 18.7; S, 21.3%). Its mixture with 1-aminobenzthiazole commenced to soften at 120° and melted indefinitely at about 127°. On treating the base with hydrochloric acid the red hydrochloride was at once regenerated.

*ψ-Amino-3-toluthiazole Hydrochloride.*—The hydrochloride from 1 g. of 1-amino-3-methylbenzthiazole (p. 1398) was suspended in 25 c.c. of alcohol and treated with 3 c.c. of ethyl nitrite solution. A *hydrochloride* was obtained as in the previous case in ruby-red prisms which sintered at 140° and showed colour change at 145° (Found: Cl, 18.0.  $C_7H_8N_2ClS$  requires Cl, 18.7%). On treatment with ammonia a base similar to the previous one was obtained.

*ψ-Amino-5-toluthiazole hydrochloride* was obtained from 1-amino-5-methylbenzthiazole in red prisms which sintered at 130°, darkened at 140° and softened at about 150°.

#### *The Mobility of 5-Bromo-1-aminobenzthiazole.*

*5-Bromo-1-aminobenzthiazole dibromide*, prepared from *p*-bromophenylthiocarbamide (1 g.) and bromine (0.8 c.c.) in chloroform (10 c.c.) in the usual way, separated, on cooling, as a red gum which solidified in orange-red needles, softening at 80—82° (Found: Br, 63.5.  $C_7H_5N_2Br_2S$  requires Br, 61.7%). By successive treatment with sulphurous acid and ammonia it was converted into 5-bromo-1-aminobenzthiazole, m. p. 211°, identical with the bromo-substitution product obtained by dissolving 1-aminobenzthiazole dibromide in hot water (Hugershoff, *loc. cit.*).

*1-Acetylaminobenzthiazole Hexabromide.*—1-Acetylaminobenzthiazole (0.5 g.) in chloroform (6 c.c.) was slowly treated with

bromine (0.4 c.c.), and the solution boiled after some time. The *hexabromide* crystallised from the warm liquid, on scratching, in small, orange-red prisms which, after being dried, turned yellow at 130°, lost bromine at about 140°, and became colourless at about 160° (Found: Br, 71.6.  $C_9H_5ON_2Br_6S$  requires Br, 71.4%).

*5-Bromo-1-acetylaminobenzthiazole*.—A solution of the preceding hexabromide in alcohol was diluted with a little water and concentrated. The white, crystalline product, after treatment with dilute ammonia, crystallised from ethyl acetate in prisms, m. p. 223° (Found: Br, 30.0.  $C_9H_7ON_2BrS$  requires Br, 29.5%). On hydrolysis with 50% sulphuric acid, impure 5-bromo-1-aminobenzthiazole (m. p. 184°) was obtained which melted at 198° when mixed with an authentic specimen.

*5-Bromo-1-imino-2-acetyl-1:2-dihydrobenzthiazole*.—A solution of the dibromo-addition compound of 1-imino-2-acetyl-1:2-dihydrobenzthiazole in alcohol was diluted with water, concentrated on a steam-bath, decanted from a small purple residue, and evaporated. The resin thus obtained became hard on treatment with ammonia and thereafter crystallised from alcohol-ethyl acetate in small plates, m. p. 199–200° (Found: Br, 30.0.  $C_9H_7ON_2BrS$  requires Br, 29.5%).

On hydrolysis with 40% sulphuric acid and neutralisation, 5-bromo-1-aminobenzthiazole (m. p. 204°) was obtained; this crystallised from alcohol in prisms which, alone or mixed with 5-bromo-1-aminobenzthiazole prepared from 1-aminobenzthiazole dibromide, melted at 210°.

#### *Homologues of 1-Aminobenzthiazole.*

*1-Amino-3-methylbenzthiazole Dibromide*.—The solution obtained by treating 2 g. of *o*-tolylthiocarbamide in 20 c.c. of chloroform with bromine (1.5 c.c.) was refluxed and concentrated; on cooling, lustrous orange plates of the *dibromide* crystallised, m. p. 110° (effervescence) (Found: Br, 49.6.  $C_8H_5N_2Br_2S$  requires Br, 49.4%). The dibromide was unstable and decomposed with loss of bromine on exposure to air. It dissolved in alcohol, and from the solution, diluted with water and thereafter concentrated, white needles of the *hydrobromide* of bromo-1-amino-3-methylbenzthiazole were obtained which became yellow at 260° and charred at about 290° (Found: Br, 49.8.  $C_8H_7N_2BrS \cdot HBr$  requires Br, 49.7%). The *base* obtained by treating the hydrobromide with ammonia separated from alcohol-ethyl acetate in tufts of silky needles, m. p. 212° (Found: Br, 33.1.  $C_8H_7N_2BrS$  requires Br, 32.9%).

*1-Amino-3-methylbenzthiazole* was obtained from the dibromide by reduction with sulphurous acid and sulphur dioxide in the usual

way. It crystallised from 50% alcohol in small, lustrous plates, m. p.  $136^{\circ}$ , and resembled 1-aminobenzthiazole in odour (Found: S, 19.8.  $C_8H_8N_2S$  requires S, 19.5%). The diazotised base gave a red azo-dye on coupling with alkaline  $\beta$ -naphthol.

*1-Amino-5-methylbenzthiazole Dibromide Hydrobromide.*—*p*-Tolylthiocarbamide (2 g.) was brominated in chloroform as in the previous case. The bromo-addition compound was obtained in small, glistening orange-red prisms, m. p.  $134^{\circ}$  (decomp.) after sintering at  $128^{\circ}$  (Found: Br, 59.0.  $C_8H_8N_2Br_2S \cdot HBr$  requires Br, 59.2%). The tribromide was very unstable in air. Treatment of its alcoholic solution with water produced the hydrobromide of the bromo-substitution derivative, which crystallised in silky needles. The base obtained by treatment with ammonia crystallised from alcohol (80%) in small prisms, m. p.  $210^{\circ}$  (Found: Br, 33.0.  $C_8H_7N_2BrS$  requires Br, 32.9%).

By brominating *p*-tolylthiocarbamide (1 g.) in chloroform under similar conditions to the above, the tribromide was on one occasion obtained in bright red prisms, m. p.  $106^{\circ}$  (decomp.) (Found: Br, 59.5%).

*1-Amino-5-methylbenzthiazole*, obtained by reduction of the tribromide, crystallised from 50% alcohol in small, glistening prisms, m. p.  $142^{\circ}$ , having the usual faint odour of these bases (Found: S, 19.1.  $C_8H_8N_2S$  requires S, 19.5%). The base yielded an unstable diazonium chloride which coupled with alkaline  $\beta$ -naphthol, giving a red azo-dye of the usual type.

*1-Amino-4-methylbenzthiazole Tetrabromide.*—Prepared from *m*-tolylthiocarbamide (0.3 g.) and bromine (0.4 c.c.) in chloroform (5 c.c.) in the usual way, the *tetrabromide* was obtained, either spontaneously or by cooling the solution and scratching, in slender, orange-red needles which, after being dried, became yellow at  $140^{\circ}$ , soft at  $160^{\circ}$ , white at  $180^{\circ}$ , brown at  $210^{\circ}$ , and melted and decomposed at about  $250^{\circ}$  (Found: Br, 66.8.  $C_8H_8N_2Br_4S$  requires Br, 66.1%). It had the usual properties of these bromides.

*1-Amino-4-methylbenzthiazole.*—The *tetrabromide* was reduced in the usual way. The base was precipitated by making the sulphurous acid solution alkaline and a further small quantity was obtained by extracting the filtrate with ether. The base crystallised from 50% alcohol in pearly plates, m. p.  $145^{\circ}$  (sintering at  $135^{\circ}$ ), having the faint characteristic odour of these compounds (Found: S, 19.2.  $C_8H_8N_2S$  requires S, 19.5%).

*1-Amino-3 : 5-dimethylbenzthiazole Tetrabromide.*—Prepared from 1 g. of *m*-xylylthiocarbamide and bromine (0.8 c.c.) in chloroform (10 c.c.), the *tetrabromide* separated from the cooled solution in red flakes which, after being dried in a vacuum, became colourless at

80—90° and were unmelted at 250° (Found: Br, 63.8.  $C_9H_{10}N_2Br_4S$  requires Br, 64.3%). It is very unstable, losing bromine and becoming colourless on exposure to air for  $\frac{1}{2}$  hour.

1-Amino-3:5-dimethylbenzthiazole, obtained from it in the usual way, crystallised from ether in needles and thereafter from dilute alcohol in silvery plates, m. p. 116° (softening at about 100°), having the usual faint odour of these compounds (Found: S, 16.8.  $C_9H_{10}N_2S$  requires S, 17.9%).

2-Amino- $\beta$ -naphthathiazole Tetrabromide.—Prepared from  $\alpha$ -naphthylthiocarbamide (0.5 g.) and bromine (0.5 c.c.) in chloroform, the tetrabromide was obtained as an orange, microcrystalline powder which, after drying in a vacuum, began to lighten in colour at 130° and was unmelted at 260° (Found: Br, 60.9.  $C_{11}H_8N_2Br_4S$  requires Br, 61.6%).

2-Amino- $\beta$ -naphthathiazole, obtained by reducing the tetrabromide, crystallised from alcohol-ethyl acetate in small, odourless crystals, m. p. 235—237° after sintering at about 220° (Found: S, 16.1.  $C_{11}H_8N_2S$  requires S, 16.0%).

2-Amino- $\alpha$ -naphthathiazole Tetrabromide.— $\beta$ -Naphthylthiocarbamide (0.5 g.) was brominated as in the case of the  $\alpha$ -compound. The tetrabromide was obtained as a yellow, microcrystalline powder, m. p. 165° (decomp.) (Found: Br, 60.8%).

2-Amino- $\alpha$ -naphthathiazole crystallised from alcohol-ethyl acetate in small prisms, m. p. 249—251°, after sintering at about 230° (Found: S, 16.2.  $C_{11}H_8N_2S$  requires S, 16.0%).

*The 1-Aminobenzthiazole Dibromide  $\rightarrow$  5-Bromo-1-aminobenzthiazole Hydrobromide Transformation.*

1-Aminobenzthiazole dibromide (obtained by Hugershoff's method, *loc. cit.*; after being dried in the usual way, it turned red at 105—110°, melted at 112—114°, and charred at 206°) (36 g.) was added to 200 c.c. of nearly boiling water. A colourless solution was at once produced which on evaporation on the steam-bath left 32 g. of crude 5-bromo-1-aminobenzthiazole hydrobromide (a certain amount of the dibromide undergoes decomposition, giving the hydrobromide of 1-aminobenzthiazole). Thirty g. of the product, after treatment with ammonia and recrystallisation from alcohol, yielded 15—16 g. of 5-bromo-1-aminobenzthiazole.

In view of the curious physiological action of certain benzthiazole derivatives (J., 1925, 127, 911), the "alleged immunity to certain swamp fevers conferred by "thiazole dermatitis" (private communication from Dr. G. M. Dyson), and the clinical use of substances such as *o*-aminophenyl sulphide in syphilis, a series of

experiments has been commenced in collaboration with Dr. Dyson on the trypanocidal effect of water-soluble aminobenzthiazoles.

The author desires to express his gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in these experiments, and to the Trustees of the Dixon Fund of the University of London for a grant which has defrayed the cost of some of the materials.

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### CLXXX.—*Aminobenzthiazoles. Part IV. The Stability of the Bromides of the 1-Xylidinodimethylbenzthiazoles.*

By ROBERT FERGUS HUNTER.

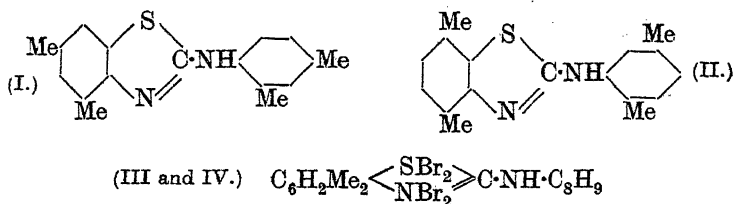
THE remarkable instability of 1-amino-3 : 5-dimethylbenzthiazole tetrabromide (this vol., p. 1389) must be attributed to the combined effects of the *o*- and *p*-methyl groups, since the stability of the bromo-addition compounds of 1-amino-5-methylbenzthiazole, 1-amino-3-methylbenzthiazole, and 1-amino-3 : 5-dimethylbenzthiazole decreases in the order given. The *o*-methyl group is mainly responsible for the instability, a fact which is further exemplified by the relative stabilities of the bromides of 1-*o*-toluidino-3-methylbenzthiazole and 1-*p*-toluidino-5-methylbenzthiazole (Hunter, J., 1925, 127, 2023).

It was therefore of interest to examine the effect of replacing the amino-group in 1-amino-3 : 5-dimethylbenzthiazole by an arylamino-group. In the first place, it might be expected on *a priori* grounds that the residual affinity of the aromatic nucleus of the arylamino-group would exert a stabilising influence on the bromo-addition compound of such a base, and secondly, on the basis of Ingold's modified strain theory (J., 1921, 119, 305 and later papers),\* the bulky substituent might be expected to enhance the arylamino-

\* The theoretical basis of this theory will be discussed in a paper dealing with the mobility of the 5-bromo-1-alkylaminobenzthiazole system and the addition of bromine to tautomeric systems of this type. The unsaturation of the ring nitrogen atom of the mobile triad system  $N:C-N[H] \rightleftharpoons N[H]:C-NX$  is profoundly affected by the mobility or potential mobility of the tautomeric hydrogen atom. For instance, there is a striking increase in the stability of the 5-bromo-1-alkylaminobenzthiazole 2 : 2-dibromide towards hydriodic acid as the alkyl group is in turn ethyl, *n*-propyl, *n*-butyl, and *isobutyl*. In this connexion it is hoped to obtain some information on the deflexion of the carbon tetrahedral angle (Deshapande and Thorpe, J., 1922, 121, 1430, and later papers) produced by the hitherto unstudied butyl, amyl, and hexyl groups.

phase of the mobile aminothiazole system (this vol., p. 1385) the ring nitrogen atom in which is more unsaturated than that in the 1-imino-1:2-dihydrothiazole form. The second effect also, owing to the nitrogen atom being the centre of unsaturation in a thiazole ring (this vol., p. 538), would increase considerably the stability of the bromo-addition compound.

The bromides of the 1-xylidinodimethylbenzthiazoles (I and II) were therefore studied and it was found that the 1-xylidino-group had a most striking stabilising effect on the aminobenzthiazole bromide complex.



Under the usual conditions of bromination in chloroform (*loc. cit.*), *s*-di-*m*-xylylthiocarbamide readily passed into the *tetrabromide* of 1-*m*-xylidino-3:5-dimethylbenzthiazole (III), which is one of the most stable compounds of this type so far isolated, its stability in air being of the same order as that of the 2-β-naphthylamino-α-naphthathiazole bromides (J., 1925, 127, 2270). The formation, in the presence of an excess of halogen, of a labile *heptabromo*-addition compound of the dimethylbenzthiazole was also observed, this compound being doubtless the hydrobromide of the hexabromo-addition compound, which was on one occasion isolated in an impure condition. These compounds were all reduced in the usual manner by sulphurous acid, yielding the xyloidinodimethylbenzthiazole (I).

While these experiments were in progress, a paper by Levi (*Atti Cong. Naz. Chim. Ind.*, 1924, 400) appeared, in which 1-*m*-xylidino-3:5-dimethylbenzthiazole (I) was described as being formed by the thionation of a mixture of *m*-xylidine and phenyl-*m*-xylylthiocarbamide. Levi's product, however, although it gave the pure acetyl derivative, must have been very impure, because the melting point recorded is nearly 20° too low. This is not so surprising in view of the difficulties involved in such preparations (Hunter, *J. Soc. Chem. Ind.*, 1923, 42, 302T).

Under the usual conditions of bromination, *s*-di-*p*-xylylthiocarbamide readily passed into the *tetrabromide* of 1-*p*-xylidino-3:6-dimethylbenzthiazole (IV), a bright red compound resembling the *m*-xylidino-isomeride in stability and other properties.



None of the 1-xylidinodimethylbenzthiazole bromides gave any evidence whatsoever of the existence of stable yellow tribromides (*loc. cit.*). Therefore, with regard to stability in the air, the 1-arylaminobenzthiazole bromides fall into two groups, the first of which includes the labile red bromo-addition compounds, such as those derived from 1-anilinobenzthiazole and its tolyl and  $\alpha$ -naphthyl homologues, which on exposure to air evolve bromine and pass into stable yellow tribromides; and the second of which includes the stable red bromides of 2- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole and of the 1-xylidinodimethylbenzthiazoles described in this paper, which lose bromine appreciably only on prolonged exposure to moist air and do not appear to be capable of yielding yellow tribromides.

#### EXPERIMENTAL.

**1-m-Xylidino-3 : 5-dimethylbenzthiazole Hexabromide Hydrobromide.**—A solution of 1 g. of *s*-di-*m*-xylylthiocarbamide in chloroform (10 c.c.) was gradually treated with a solution of bromine (1 c.c., in chloroform, 3 c.c.) and then heated under reflux for 2 minutes, cooled, and a part of the solvent evaporated off in a vacuum at 15°. The red gum produced, which solidified, was triturated with an ethereal solution of bromine; the *heptabromide* was then obtained in small, red prisms which, after drying in a vacuum over potassium hydroxide, sintered at 153° and melted at 158° (decomp.) (Found: Br, 66·7.  $C_{17}H_{18}N_2Br_6S \cdot HBr$  requires Br, 66·7%).

**1-m-Xylidino-3 : 5-dimethylbenzthiazole Tetrabromide (III).**—The dixylylthiocarbamide (5 g. in chloroform, 10 c.c.) was treated as above (bromine, 4·8 c.c., in chloroform, 10 c.c.) and the cooled solution allowed to crystallise in a vacuum; the *tetrabromide* was then obtained in small, orange-red crystals which, after being washed with bromine in ether and dried in a vacuum, melted at 130° (decomp.) (Found: Br, 52·7.  $C_{17}H_{18}N_2Br_4S$  requires Br, 53·3%). The tetrabromide had the usual properties of these compounds, being reduced by hydriodic acid with liberation of iodine, and evolving acetaldehyde on boiling with dilute alcohol.

Bromination in similar circumstances of 5 g. of the thiocarbamide with 5 c.c. of bromine produced on one occasion a red gum which, on trituration with bromine in ether, solidified to a mass of small, red crystals, m. p. 126° after drying in a vacuum (Found: Br, 61·3.  $C_{17}H_{18}N_2Br_6S$  requires Br, 62·9%).

1-m-Xylidino-3 : 5-dimethylbenzthiazole obtained in the usual way by reducing any of the bromides with sulphurous acid and sulphur dioxide (*loc. cit.*) and liberating the base with ammonia, crystallised from alcohol-ethyl acetate (1 : 1) in large flakes and thereafter

from light petroleum (b. p. 40—60°) in small prisms, both forms melting at 175° (Found : S, 11.4. Calc. : S, 11.4%).

The acetyl derivative, obtained by heating a solution of the base in acetic anhydride for a few minutes and pouring it into alcohol, slowly crystallised in large prisms, m. p. 131—132° after recrystallisation from alcohol (Levi, *loc. cit.*, gives m. p. 131°).

*s-Di-p-xylylthiocarbamide*.—A mixture of technical *p*-xylydine (18 g.), alcohol (27 c.c.), carbon disulphide (33 c.c.), and potassium hydroxide (4 g.) was heated for 2—3 hours, and the product worked up in the usual way; on recrystallisation from alcohol the thiocarbamide was obtained in needles, m. p. 146—147° (Dyson and George, J., 1924, 125, 1705, give the m. p. as 148.5°). The yield was about 50%.

*1-p-Xylidino-3 : 6-dimethylbenzthiazole Tetrabromide* (IV).—*Di-p-xylylthiocarbamide* (1.25 g.) in chloroform was treated with bromine (1.2 c.c.) in chloroform (2.5 c.c.) in the usual way, the solution concentrated in a vacuum, and the product triturated with an ethereal solution of bromine. The red oil obtained, on partial evaporation of the ether, solidified to a mass of small, red crystals of the *tetrabromide* which were washed with chloroform and dried in a vacuum in the usual way. They had the usual properties and charred above 200° (Found : Br, 53.6.  $C_{17}H_{18}N_2Br_4S$  requires Br, 53.2%).

*1-p-Xylidino-3 : 6-dimethylbenzthiazole*, obtained by the reduction of the *tetrabromide* in the usual way, crystallised from ethyl acetate in small prisms, m. p. 200° (Found : S, 11.6.  $C_{17}H_{18}N_2S$  requires S, 11.4%).

In conclusion, the author desires to express his gratitude to Professor J. F. Thorpe, F.R.S., for his kind interest in this work, and to Mr. G. G. Alford for carrying out some of the experiments. A part of the expense of the materials was defrayed by a grant for which the author is indebted to the Trustees of the Dixon Fund of the University of London.

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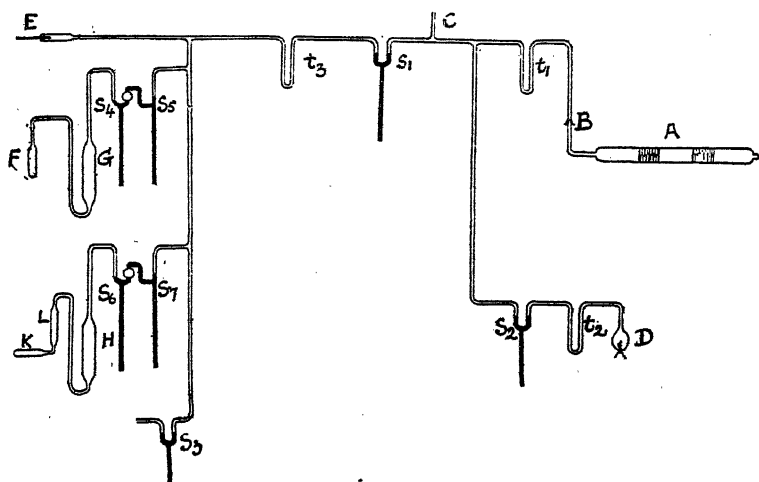
## CLXXXI.—*The Direct Synthesis of Nitrous Oxide.*

By DAVID LEONARD CHAPMAN, RICHARD ALLEN GOODMAN, and  
RODNEY THOMAS SHEPHERD.

HITHERTO it has not been found possible to effect a direct synthesis of nitrous oxide. We shall show that this compound is slowly formed when an electric discharge is passed through nitrogen at low

pressure in a quartz tube into the walls of which oxygen has previously been driven by means of the discharge, and can be isolated as it is formed by condensing it in a U-tube surrounded by liquid air. When completely decomposed by heating a platinum wire in it, the volume increases in the ratio 2 to 3, the proportion of nitrogen to oxygen in the decomposition products being 2 to 1.

The quartz tube, A (*vide* diagram), in which the discharge took place was approximately 1 m. in length and 1180 c.c. in volume. The rest of the apparatus was of glass, and was connected to the quartz tube by a ground glass joint, B, which was lubricated with glacial phosphoric acid and sealed by mercury. The long U-tube,  $t_1$ , could be immersed in liquid air when desired, and served the



double purpose of keeping back mercury vapour and of condensing the nitrous oxide. A T-piece, C, led to the McLeod gauge used to measure the pressures. The discharge tube, with gauge and liquid-air trap, could be shut off from the rest of the apparatus by the mercury seals  $s_1$  and  $s_2$ . The seal,  $s_2$ , served to put the quartz tube into communication with a U-tube,  $t_2$ , and a bulb, D, which contained a spiral of fine platinum wire welded to thick platinum leads, which passed to the outside through a lead-glass seal.  $t_3$  was another U-tube which could be surrounded by liquid air. Beyond the mercury seal,  $s_3$ , was a mercury vapour pump and an auxiliary Sprengel pump. The remainder of the apparatus was for the purpose of generating and storing the gases required.

*Hydrogen.*—The hydrogen required for the analysis was admitted to the apparatus by diffusion through the walls of a platinum tube, E, sealed into the end of a glass tube. The platinum tube was heated

to redness in an atmosphere of hydrogen, prepared in the ordinary way in a small Kipp's apparatus from zinc and dilute sulphuric acid. The gas, after bubbling through a solution of caustic soda, was passed through a quartz tube which surrounded the platinum tube. To admit hydrogen to the apparatus the quartz tube was heated strongly.

*Nitrogen.*—The nitrogen was prepared by the decomposition of pure anhydrous barium azide contained in a vertical tube, F. This was connected to a reservoir, G, of capacity about 400 c.c., in which the gas was stored. One limb of the seal  $s_4$  was blown out into a bulb, of volume about 4 c.c., the upper end being connected by millimetre capillary tubing to another seal,  $s_5$ . This arrangement was employed to withdraw small amounts of gas from the reservoir, in which the pressure was about 1 cm., in the following way. The mercury in the seal  $s_4$  was lowered, and when raised again, shut off a small amount of gas in the bulb. The seal  $s_5$  was then lowered until the T-piece was just cleared. The mercury in  $s_4$  was then raised, and the gas enclosed in the bulb driven past the seal  $s_5$  into the apparatus. By subsequently lowering the mercury in the seal  $s_4$ , the bulb could be again evacuated. The tube, F, containing the barium azide, was heated in a small bath of glycerol. The nitrogen was evolved at a convenient rate at  $152^\circ$ .

*Oxygen.*—The oxygen was prepared by the thermal decomposition of recrystallised potassium permanganate contained in the tube K. The gas passed up a tower, L, containing solid caustic potash to absorb any carbon dioxide. L was connected to a reservoir, H, and two seals,  $s_6$  and  $s_7$ , by means of which small quantities of gas could be removed as described above in the case of nitrogen.

The gases were not admitted to the discharge tube until they had remained in that portion of the apparatus between the seals  $s_1$ ,  $s_3$ ,  $s_5$ ,  $s_7$ , for at least  $\frac{1}{2}$  hour with liquid air surrounding the U-tube  $t_3$ . The gases did not come into contact with any grease taps whatever.

*The Discharge.*—For the purpose of exciting the discharge, two pieces of aluminium foil about 6 cm. wide were fastened by copper wire round the tube at equal distances from each end and from each other. The aluminium electrodes were connected by means of copper wire with the secondary of a 10-inch induction coil, which was run from the 100-volt mains, a resistance keeping the primary current constant at about  $2\frac{1}{4}$  amp. Interruption of the primary was effected by a mercury break of the simple dipper type. The dipper was oscillated by means of an eccentric coupled directly to the shaft of an electric motor. By this means constant interruption was obtained. There was an external spark-gap of 1 cm.

To conduct an experiment, the whole apparatus was first

thoroughly evacuated, all the tubing, including the McLeod gauge, being heated twice with a blow-pipe flame, in order to drive off gases retained by the surface of the glass. The quartz tube was thoroughly heated to redness, section by section, to expel any gas that might be absorbed. The required amount of oxygen was then withdrawn from the reservoir, and admitted to the quartz tube in the manner already described. The initial pressure of oxygen was about 0.08 mm. The pressures recorded below have been reduced to the temperature of 18°, allowance being made for the cooling effect of the liquid air on the small proportion of gas contained in the U-tube  $t_1$ . After the discharge had been started, the progress of the absorption was followed by measuring the pressure at convenient intervals of time. The discharge was stopped when the pressure-time curve had become very flat. The liquid air was then removed, and the tube evacuated. Nitrogen was then admitted to a pressure of about 0.08 mm., the liquid air replaced round  $t_1$ , and the discharge again started. From time to time the discharge was stopped, and the pressure measured both with and without liquid air surrounding the U-tube  $t_1$ . The difference between these two pressures gave the amount of condensable gas formed. It was, of course, produced at a gradually decreasing rate. The results of four experiments are in Table I.

TABLE I.

Oxygen absorbed.	Nitrogen absorbed.	Condensable gas.	Duration.
0.01669 mm.	0.03777 mm.	0.01688 mm.	6½ hrs.
0.02168	0.04282	0.02321	9½
0.01576	0.04725	0.02999	11½
0.01479	0.04869	0.02185	17½

When a convenient amount of gas had been obtained, the tube was evacuated, the liquid air remaining round the U-tube. A small amount of the condensable gas was always lost during this operation, showing that the liquid had an appreciable vapour pressure at the temperature of liquid air. Some experiments were made with a view to determining the properties of the gas. It was quite stable, and could be kept for any length of time. It was very rapidly destroyed by the discharge, decomposition being complete in about 5 seconds. The observed expansion was dependent on the length of time during which the discharge passed, a maximum being reached in a few seconds. The contraction which followed the expansion was probably mainly due to combination of the oxygen produced in the decomposition with mercury vapour, in the presence of which this experiment had to be performed. The gas was not condensed when the U-tube was surrounded by solid carbon dioxide and ether. It did not react with oxygen when left to stand with this

gas, showing that it could not be nitric oxide. This conclusion was confirmed by the circumstance that the gas did not attack the mercury in the McLeod gauge either before or after it had been mixed with oxygen.

*Analysis.*—The gas was analysed in the following way. The mercury seal  $s_2$  was opened, and the pressure of the gas in the whole of the apparatus to the right of the seal  $s_1$  measured. Liquid air was then placed round the U-tube  $t_2$ , and when all the gas had condensed,  $s_2$  was closed. The liquid air was then removed, and replaced by solid carbon dioxide and ether, in order that the decomposition might be carried out in the presence of as little mercury vapour as possible. The platinum spiral was then heated to bright redness. After some hours the heating was stopped and the bulb allowed to cool. The flask containing the solid carbon dioxide and ether was removed, the seal  $s_2$  opened, and the pressure measured both with and without liquid air surrounding the U-tube  $t_1$ . The difference between these two measurements gave the amount of condensable gas undecomposed. The difference between this and the amount originally present represented the gas decomposed. The results are in Table II.

TABLE II.

	Mm.
Pressure after decomposition, with liquid air .....	0.03746
Pressure after decomposition, without liquid air .....	0.03948
Condensable gas undecomposed .....	0.00202
Initial amount of condensable gas .....	0.02661
Condensable gas decomposed .....	0.02459
Expansion on decomposition .....	0.01287

It will be seen that, within the limits of experimental error, the expansion is equal to half the amount of condensable gas decomposed.

The next analysis was made in such a way as to enable the amount of oxygen produced by the decomposition to be determined. When this was known, the relative proportions of oxygen and nitrogen in the condensable gas could be calculated.

The ratio of the volume of the quartz tube *plus* tubing up to the seals  $s_1$  and  $s_2$ , to the total volume when  $s_2$  was opened, was first determined by measuring the pressure of the same amount of gas in the two volumes. The decomposition was then carried out in the same manner as before. While this was proceeding, hydrogen was admitted to the quartz tube, and its pressure measured. From the ratio of the volumes, the pressure this gas would produce in the total volume when  $s_2$  was opened was calculated. After decomposition, the mercury in  $s_2$  was lowered, and the pressure measured, as in the former case, with and without liquid air surrounding the

U-tube  $t_1$ . The pressure of the products of decomposition was found by subtracting the pressure of the hydrogen from the total pressure measured after decomposition with liquid air surrounding the U-tube.  $t_2$  was then immersed in liquid air, and the spiral heated for several hours until no further fall in pressure occurred. From the contraction due to the formation of water, the amount of oxygen present was deduced. The nitrogen was found by difference. The results are in Table III.

TABLE III.

(a) *Expansion on decomposition.*

	Mm.
Pressure after decomposition, with liquid air .....	0.05998
Pressure after decomposition, without liquid air .....	0.06064
Condensable gas undecomposed .....	0.00066
Initial amount of condensable gas .....	0.02156
Condensable gas decomposed .....	0.02090
Pressure of hydrogen admitted to quartz tube .....	0.03001
Ratio of volumes, quartz tube : total .....	0.9719
Pressure of hydrogen in total volume .....	0.02917
Pressure of nitrogen, hydrogen, and oxygen .....	0.05998
Pressure of products of decomposition .....	0.03081
Expansion produced by decomposition .....	0.00991

(b) *Estimation of oxygen.*

Initial pressure (hydrogen, nitrogen, and oxygen) .....	0.05998
Final pressure (excess hydrogen and nitrogen) .....	0.02891
Contraction .....	0.03107
Amount of oxygen required for this contraction .....	0.01036

(c) *Summary.*

Condensable gas decomposed .....	0.02090
Oxygen produced .....	0.01036
Nitrogen produced .....	0.02045

The expansion produced on decomposition is again seen to be half the amount of condensable gas destroyed, and the ratio of nitrogen to oxygen in the products is 2 to 1, leaving no doubt that the gas was nitrous oxide.

In experiments not described above, a small proportion of oxygen was added to nitrogen in the discharge tube. Even when the partial pressure of the oxygen was as small as one-tenth of that of the nitrogen, nitrogen peroxide was produced.

## CLXXXII.—*Resins in Coal. Studies in the Composition of Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

WE have shown (J., 1925, 127, 112) that bituminous coal consists essentially of ulmin compounds in which morphologically organised plant-tissues, that have escaped ulmification, are dispersed. The ulmins, when first formed as the products of mouldering decay of vegetable matter, are characterised by ready solubility in alkaline solutions, but their derivatives, in the condition in which they normally exist in bituminous coal, are insoluble. Solubility in alkaline solutions can, however, be conferred on the ulmin compounds of bituminous coal by such mild oxidation as is afforded by treatment with air at low temperatures (up to 150°) or with hydrogen peroxide. The soluble ulmins so produced, which we have termed "regenerated" ulmins, are not identical in character with the insoluble ulmins in newly-won bituminous coal, for the external groupings of the molecules are modified during oxidation, the more easily detached being eliminated to form simple oxygenated compounds, with the substitution of carboxylic groupings which render the residue definitely acidic in character. The nuclear structure, however, remains unaffected. This nucleus we have shown (J., 1925, 127, 2236) to be built up of compact systems of benzenoid groupings connected together by heterocyclic structures, such as pyrrole and furan or their derivatives.

The bulk of bituminous coal consists of ulmins having molecular structures of this character. In banded bituminous coals, such as constitute the majority of British coals, the dull (durain) bands contain a proportion, usually between 20 and 30%, of morphologically organised plant entities, amongst which spore exines and cuticles predominate, that have undergone but little change from their original condition during the processes of decay suffered by the accumulations of plant material from which the coal was formed. Of the bright portions of coal, the clarain contains but small proportions, up to about 5%, of such plant entities, whilst the vitrain contains none.

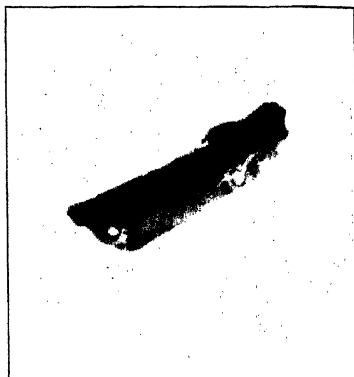
In our previous papers we noted that, for the sake of simplicity, the existence in coal of natural plant substances devoid of morphological organisation, such as "resins," could be ignored, but expressed the intention of dealing with these substances separately. In order to do so, it is necessary for us to enlarge on the statement, contained in a footnote to our paper on the constitution of the coal ulmins (*loc. cit.*, p. 2236), regarding the character of vitrains; for the







× 330



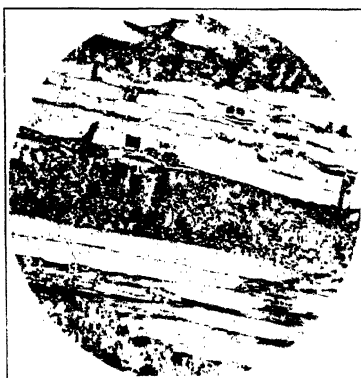
× 330

FIG. 1.



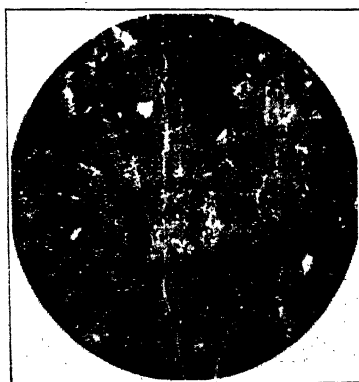
× 130

FIG. 2.



× 130

FIG. 3.



× 150

existence of resins in a bituminous coal is best revealed in the vitrain portion.

The vitrain portion of a banded bituminous coal has for long been considered by British investigators to be essentially structureless, having been so qualified in Stopes's original descriptions of the banded ingredients of bituminous coal (*Proc. Roy. Soc.*, 1919, *B*, 90, 470), based largely on an examination of transparent sections. Partly through the use of a new method of examining, by reflected light, coal surfaces that have been polished and etched, and partly as the result of the remarkably fine technique for the preparation of transparent sections of coal developed by Dr. R. Thiessen, of the United States Bureau of Mines, who has been good enough to prepare for us sections of a number of specimens of vitrain from British coals, it is now realised that a completely structureless vitrain, if it exists at all, is a rarity.

A description of the structures to be observed in most vitrains is reserved for another communication. It will suffice here to state that, in all of the many examples of vitrain that we have examined, the appearance of plant cells, usually derived from cortical tissues, can be disclosed. We purposely refer to the "appearance" of plant cells, because these structures cannot be separated from the coal mass intact and preserved, as can the cuticles and spore exines, and it is clear that, being ulmins, they are pseudomorphs of the original structures.

For the work described in this paper, vitrain from the Hamstead coal, which we have used for much of our previous work, was chosen because its oxidation by hydrogen peroxide could readily be controlled. During a carefully regulated oxidation of Hamstead vitrain, the soluble "regenerated" ulmins being removed from time to time by means of dilute sodium hydroxide solution, it was found that, when but little residue remained, the particles began to assume distinctive shapes. Some of the particles had the appearance of fibre cells, whilst in a few the shapes of tracheids, showing bordered pits, could be observed. All such shapes were, however, transient, disappearing as the ulmins dissolved. Nevertheless we were able to secure examples and retain them long enough to photograph them under the microscope. Some are reproduced in Fig. 1.

The fragments to which, from the point of view of the present paper, the greater interest attaches, were dark-coloured and elongated. They were usually ribbed along their major axes and had clean-cut ends. On persisting with the action of hydrogen peroxide, followed by treatment with sodium hydroxide solution, these fragments became gradually lighter in colour and finally, when all the ulmins had been removed, appeared as yellow rods varying in length

up to 0.02 inch. Their diameter was about one-tenth of their length.

From their general character and from the cellular appearance of the ulmin material surrounding them, there seems little doubt but that these rods were resin inclusions. A number of them were collected and extracted in a Soxhlet fat-extraction apparatus with chloroform, in which they were almost completely soluble, when a dark yellow semi-solid extract was obtained. The analytical results (Found: C, 80.6; H, 10.3%) are consistent with the assumption that the material was a resin.

Confirmation of the suggestion that the resin rods existed in this sample of Hamstead vitrain in the position that they had occupied in the woody tissues from which the vitrain was formed is obtainable from photomicrographs of portions of the same sample of vitrain as was used for the oxidation experiments, polished and etched with chromic and sulphuric acids. Two such photographs are reproduced in Figs. 2 and 3, the magnification in each instance being 130 diameters. In Fig. 2, the surface is at right angles to, and in Fig. 3 it is parallel with, the cell-walls. The resin inclusions appear as circular patches in Fig. 2 and as rods in Fig. 3.

The cellular structure that abounds in vitrain—in the present example it is of xylem—can be clearly seen in the photographs, and it may well be asked how such structures could have escaped notice. Although they are readily rendered visible by polishing and etching a vitrain surface, a method of examination that has but recently come into use, the structures are difficult to detect in a transparent section viewed by transmitted light, because they are not outlined on the transparent reddish-brown background by a contrasting colour, but are faintly visible (and then only when the section is exceedingly thin and well illuminated) by reason of slight differences in shade. For example, a photograph of a section ( $\times 150$ ) of the same sample of vitrain as was used for Fig. 2 is reproduced in Fig. 4. The circular patches so noticeable in Fig. 2 can be recognised, but no organised structures can be detected.

We are indebted to Miss M. M. Evans, of the Fuel Research Board's staff, for the preparations illustrated in Figs. 2 and 3, and to Dr. R. Thiessen for that illustrated in Fig. 4. Our thanks are also due to the Safety in Mines Research Board for permission to publish this paper.

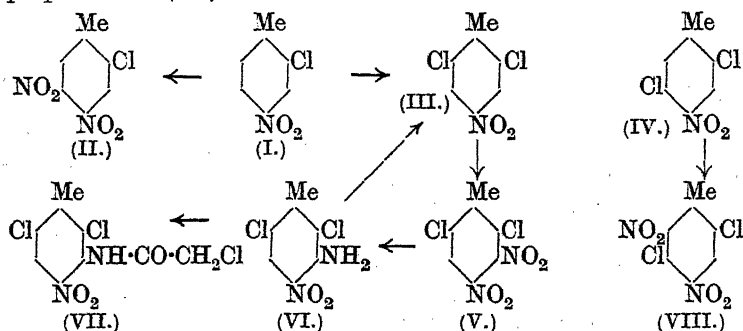
SAFETY IN MINES RESEARCH BOARD,  
SHEFFIELD.

[Received, April 22nd, 1926.]

CLXXXIII.—*A Study of the Rule of the Conservation of the Type of Substitution in Aromatic Substances.*  
*Part I. Chlorination of 2-Chloro-4-nitrotoluene.*

By WILLIAM DAVIES and GEOFFREY WINTHROP LEEPER.

MORGAN and DREW (J., 1920, 117, 793) have shown that the main product (more than 85%) of nitration of 2-chloro-4-nitrotoluene (I) is the 5-nitro-derivative (II). It was shown by one of us (J., 1922, 121, 806) that, when (I) was chlorinated in the presence of certain catalysts, not the 5- but the 6-chloro-derivative (III) was produced in a yield of more than 30%, and no other isomeride was isolated in a pure condition. It was accordingly stated (p. 806) that "it is very probable that the separation of (III) in such large amount indicates that this is the chief product." Holleman (*Chemical Reviews*, 1924, 217) quite rightly points out that (III) had not been proved to be the principal product of the reaction, and considers it possible that (IV) may occur in the residual non-crystallisable oil in such large amount as actually to be the chief product of the reaction. As changes in substitution type are of great importance both from the synthetical and the theoretical point of view, an attempt has been made to determine more accurately the proportion of (III) formed.



The more obvious lines of attack have already been investigated (Davies, *loc. cit.*, p. 810) without success. As the monochlorination product of (I) is clearly an extremely complicated mixture, the method of estimation suggested by Holleman (*loc. cit.*, p. 217) was not adopted, but instead attempts were made to convert (III) into a derivative which could be separated from the mixture by chemical means. It is to be expected that (III) would be rather more easily substituted than (IV), and the behaviour of certain reagents on (III) was accordingly examined. It was not readily sulphonated, but was quantitatively converted into the nitro-derivative (V) by

nitration under mild conditions. This could not be smoothly converted into a nitrophenol by the action of alkali under various conditions, but it was readily transformed by the action of alcoholic ammonia into (VI) (the yield of pure substance being 77%), and insufficient of the isomeric 2:6-dichloro-3-nitro-*p*-toluidine was formed to admit of its being isolated. This change is incidentally still another instance of replacement in agreement with the rule of Kenner and Parkin (J., 1920, 117, 852. See also J., 1925, 127, 2344).

2:6-Dichloro-4-nitro-*m*-toluidine (VI) has very slight basic properties and accordingly attempts were made to convert it into an acidic substance. It does not react with *p*-toluenesulphonyl chloride, and although good yields of the benzoyl and acetyl derivatives of the amine may be obtained, these compounds do not dissolve very readily in cold dilute alkali. The *chloroacetyl* derivative (VII), however, is quantitatively obtained, and easily dissolves in cold aqueous sodium hydroxide solutions, from which it is precipitated unchanged on acidification. It was hoped to be able to separate in this way (V) from (IV) or its nitro-derivative (VIII) (compare Cohen and Dakin, J., 1901, 79, 1131).

The chlorination product from (I) was therefore nitrated under the gentle conditions which were sufficient to give (V), and after the removal of the catalyst the whole product was treated with alcoholic ammonia, but it was then found that some portion of the nitration product other than (V) gave amines with ammonia with the formation of large quantities of ammonium chloride. It is possible that the 5-chlorine atom in (VIII) had, despite the steric hindrance due to the two adjacent nitro-groups, reacted with the ammonia. As the *chloroacetyl* derivatives of the amines produced were themselves soluble in alkali, this method of separation by chemical means was abandoned.

Finally, crystallisation from methylated spirit of the nitration product of the chlorination mixture was resorted to, and 2:6-dichloro-3:4-dinitrotoluene (V) was isolated in a yield corresponding to 47.9% of 2:6-dichloro-4-nitrotoluene (III) in the chlorination product. This physical method of separation, although far from being an ideal one, makes it certain, when considered in connexion with the following facts, that (III) is the chief dichloronitrotoluene formed. First, it is impossible to separate by fractional crystallisation all the (V) produced, owing to the formation of liquid and low-melting solid mixtures of a complex nature. Secondly, it has been shown (Davies, *loc. cit.*, p. 810) that the monochlorination of (I) with the calculated amount of chlorine left some unchanged substance, and therefore that one or more trichloro-*p*-nitrotoluene derivatives were formed. In fact, a larger amount of (V) can be isolated

when the chlorine absorbed is about 1% greater than the quantity theoretically required to produce dichloro-*p*-nitrotoluenes (see p. 1417). Hence the monochlorination product of (I) contains considerable quantities of substances other than dichloro-*p*-nitrotoluenes.\* Moreover, there is reason to believe that a portion of the chlorine goes into the side chain. On monochlorination of (III) in presence of either antimony trichloride or ferric chloride, a very complex mixture is formed from which nothing pure can be isolated by distillation or crystallisation, although mono-substitution could lead only to 2:5:6-trichloro-4-nitrotoluene. Nitration and reduction followed by condensation with phenanthraquinone gives only a small quantity of a phenanthrazine (m. p. 343°), which is possibly derived from 2:5:6-trichloro-4-nitrotoluene. It is certain from this experiment that the expected nuclear substitution of (III) has not occurred smoothly, and no doubt this anomalous reaction, whatever it may really be, occurs to some extent in the chlorination of the simpler 2-chloro-4-nitrotoluene. Side-chain substitution in presence of a catalyst is not so rare as is usually considered. One such instance, with 2-chloro-4-nitrotoluene, has already been pointed out (J., 1922, 121, 812), with iodine as the catalyst. The present authors find that the action of bromine on *p*-nitrotoluene at 95–120° (this relatively high temperature being necessary to bring about a reaction) gives a 46% yield of pure *p*-nitrobenzyl bromide (m. p. 99°), and a similar result with toluene in presence of antimony tribromide and bromine is recorded by van der Laan (*Rec. trav. chim.*, 1907, 26, 1).

It is difficult to advance a logical and satisfactory explanation which will account for a change of substitution type such as the one here established. As has been already pointed out (Davies, *loc. cit.*, p. 809), steric conceptions based on the atomic volumes of the groups whose positions of substitution are compared lead to contradictory conclusions, though Holleman (*loc. cit.*, p. 220) apparently considers the application of such ideas helpful as far as some rather simpler molecules are concerned. A more satisfactory, although far from convincing explanation may be found in a consideration of the difference in chemical nature of the two groups under comparison, and also in the experimental conditions of the

\* In the actual experiments herein described, *p*-nitrotoluene was dichlorinated and 2-chloro-4-nitrotoluene was not first isolated and monochlorinated (see Davies, *loc. cit.*, p. 810, for the justification of this). In any case, the other possible isomeride, 3-chloro-4-nitrotoluene, could on further chlorination give no 2:6-dichloro-*p*-nitrotoluene, and therefore the dichlorination of *p*-nitrotoluene could not, when compared with the monochlorination of 2-chloro-4-nitrotoluene, favourably affect the proportion of 2:6-dichloro-3:4-dinitrotoluene (V) actually isolated.

reactions. Investigations are being carried out with special reference to these points of view.

#### EXPERIMENTAL.

**2 : 6-Dichloro-3 : 4-dinitrotoluene (V).**—A solution of dry 2 : 6-dichloro-4-nitrotoluene (III) (6.7016 g.) in concentrated sulphuric acid (33 c.c.) at 65° is treated with a mixture of nitric acid (3.3 c.c.; *d* 1.52) and concentrated sulphuric acid (17 c.c.). The temperature is kept at 80—85° for 8 minutes. The oil that has separated then solidifies and, after drying over phosphorus pentoxide in a cathode-ray vacuum, weighs 8.1517 g. (yield 99.8%). Its m. p., 129—130°, is raised only 1° by repeated crystallisation. Further exposure to a cathode-ray vacuum causes a steady loss in weight due, as shown by a blank experiment with pure dry material, to the volatility of the substance.

The oxidisable *o*-diamine obtained by reducing 2 : 6-dichloro-3 : 4-dinitrotoluene with zinc dust in dilute alcohol containing a trace of ammonium chloride was characterised as 1 : 3-dichloro-2-methylbenzophenanthrazine, yellowish-brown plates from anisole, m. p. 279—286° (corr.), by condensation with phenanthraquinone in glacial acetic acid. The azine is sparingly soluble in cold organic solvents and develops a cerise coloration in cold concentrated sulphuric acid (Found : Cl, 19.3.  $C_{21}H_{12}N_2Cl_2$  requires Cl, 19.5%). The conversion of (V) into this compound is, however, not a quantitative process and, moreover, does not lend itself to the rough estimation of (V) in the presence of other *o*-dinitro-compounds of toluene.

**2 : 6-Dichloro-4-nitro-*m*-toluidine (VI).**—A mixture of 2 : 6-dichloro-3 : 4-dinitrotoluene (50 g.) and 200 c.c. of alcoholic ammonia (5%) is heated for  $\frac{1}{2}$  hour at 90—98° (10 atm.). The pressure is then released, 50 c.c. of alcoholic ammonia (10%) are added, and the mixture is heated for 2 hours at 127° and 7.3 atm. The product is allowed to crystallise, and after recrystallisation from alcohol 34 g. (77% yield) of the pure amine are obtained, only a small amount of low-melting material and a mere trace of ammonium chloride being produced. 2 : 6-Dichloro-4-nitro-*m*-toluidine, m. p. 136°, forms thin, deep yellow plates from benzene and brown prisms from alcohol and is soluble in mineral acids only if very concentrated (Found : Cl, 31.75.  $C_7H_6O_2N_2Cl_2$  requires Cl, 32.1%). It is different from the only other possible isomeride, 2 : 6-dichloro-3-nitro-*p*-toluidine (m. p. 130—131°; Davies, *loc. cit.*, p. 814), and is converted through its diazonium sulphate into 2 : 6-dichloro-4-nitrotoluene in good yield. Its constitution is thus established.

**2 : 6-Dichloro-4-nitroaceto-*m*-toluidide**, obtained by boiling the base



and excess of acetyl chloride in benzene for 9 hours, separates from alcohol or benzene in colourless plates, m. p.  $185^{\circ}$ . The *benzoyl* compound, similarly prepared, forms colourless, feathery crystals, m. p.  $215^{\circ}$  (Found: N, 8.7.  $C_{14}H_{10}O_3N_2Cl_2$  requires N, 8.6%). 2 : 6-Dichloro-4-nitrochloroaceto-*m*-toluidide (VII), also similarly prepared, separates from alcohol in colourless plates, m. p.  $170^{\circ}$  (Found: N, 9.4.  $C_9H_7O_3N_2Cl_3$  requires N, 9.4%).

The mixture formed by dichlorinating *p*-nitrotoluene is nitrated under the conditions described on p. 1416, the product thoroughly washed with water and heated with alcoholic ammonia under the conditions described on p. 1416. The final product, containing much ammonium chloride, and amines formed by elimination of chlorine and a nitro-group, is treated with excess of benzene, the benzene-alcohol constant-boiling mixture removed on the water-bath, the dry amine chloroacetylated in benzene, the benzene and excess of chloroacetyl chloride are removed, ultimately in a vacuum, and the chloroacetylated amines extracted with cold sodium hydroxide solution and reprecipitated with cold hydrochloric acid. The product, however, melts below  $158^{\circ}$ , and is a mixture of chloroacetylated amines, from which, after three recrystallisations from alcohol, (VII) is isolated in a quantity corresponding to a yield of less than 40% of (III).

*Estimation of 2 : 6-Dichloro-4-nitrotoluene (III) as 2 : 6-Dichloro-3 : 4-dinitrotoluene (V).*—In the preliminary experiments 1 g.-mol. (137 g.) of *p*-nitrotoluene was chlorinated in the presence of antimony trichloride until, after the removal of chlorine and hydrogen chloride, the increase in weight (69 g.) corresponded closely (within 0.2 g.) to the entry of 2 gram-atoms of chlorine. After nitration, and separation of (V) by repeated crystallisation from methylated spirit, the oily residue was distilled in steam, and the least volatile portion fractionally crystallised from alcohol. The product (2 g., m. p.  $85.5^{\circ}$ ) was shown by a mixed melting-point determination to be 2-chloro-4 : 5-dinitrotoluene (II). The yield of (V) corresponded to a yield of 43% of (III), and it was found advantageous to have a slight excess of chlorine over the 2 gram-atoms theoretically required, because the trichloronitrotoluene derivatives did not appear to interfere in the separation of (V) to the same extent as did (II).

One g.-mol. of *p*-nitrotoluene (137 g.) mixed with 4.5 g. of antimony trichloride is chlorinated at  $65$ – $75^{\circ}$  until the weight is 212.7 g. A current of dry air is blown through the liquid at  $100^{\circ}$  until all the chlorine and hydrogen chloride are removed. The increase in weight is now 0.7 g. in excess of the 69 g. theoretically required. A solution of exactly half the product (105.6 g.) in concentrated sulphuric acid (350 c.c.) is treated at  $65^{\circ}$  with a

mixture of nitric acid (20 c.c.;  $d$  1.52) and concentrated sulphuric acid (50 c.c.). Having been kept at 80–85° for 8 minutes, the mixture is poured on to ice, and kept for 48 hours at 0°. The solid product is then washed with cold water and boiled with methylated spirit (300 c.c.), the solution (A) poured off, and the residue dissolved in a further 300 c.c. of alcohol (Solution B). After 5 hours, (B) deposits almost pure (V), and the filtrate is used to dissolve the less pure crystals from (A). The deposit from (B) is recrystallised from methylated spirit, pure (V) being produced (m. p. 130–131°), and the filtrate is used to crystallise the much less pure portions; when the m. p. of these has been raised to 125–128°, they are crystallised from spirit. The process is expedited by pouring off the mother-liquor from the first crop of crystals, which contains the largest amount of (V), while the solution is hot. (V) is the least soluble substance present. In this way more than 50 g. of a pure product (m. p. 130–131°) are obtained in a very short time; further small quantities are obtained from the intermediate fractions. The large volume of solution containing the most soluble portion, when concentrated and kept for several months, deposits a solid from which a very small quantity of (V) can be isolated. In the first experiment, which lasted a week, 56.8 g. of (V) were isolated, corresponding to a yield of 45.2% of (III). In the second estimation, which, owing to the more thorough examination of the oily portions, was more prolonged, 60.1 g. [corresponding to a yield of 47.9% of (III)] were obtained and there were indications that a small quantity of (V) still remained in the oily mixture.

The semi-solid final product was recrystallised from alcohol and, apart from a large quantity of oil, two crystalline fractions, m. p. 85–97° and 100–115°, were obtained. The second substance softened at 100–101°, which is the m. p. of (VIII), but this compound could not be obtained pure. It (4 g.) was reduced as described on p. 1416, and the amine obtained was condensed with phenanthraquinone (2 g.) in boiling acetic acid. The product formed yellowish-brown needles (0.85 g.), m. p. 307–309° (decomp.; corr.), from anisole and gave a cerise coloration with cold concentrated sulphuric acid (Found: Cl, 23.6%). Whatever this compound may be, its formation shows that almost all (V) has been removed from the 100–115° fraction (about 9 g.). The high percentage of chlorine, much greater than that required for the phenanthrazines from (II) and (V), shows that probably a trichloro-nitrotoluene derivative is present.

*Chlorination of 2 : 6-Dichloro-4-nitrotoluene (III).*—This compound (41.2 g.), mixed with ferric chloride (1.8 g.), is chlorinated at 65–80°

for 24 hours, the increase in weight being 7.8 g. (calc. for monochlorination, 6.9 g.). The high temperature of 80° is ultimately required, not only to expedite the process, but also to melt the solid which crystallises out towards the end of the reaction. The product after removal of inorganic matter distils at 135—155°/5 mm. The colourless distillate is crystallised from spirit, and the portion (7 g.) which melts over the lowest range (60—78°) is nitrated with mixed sulphuric and nitric acids, the product reduced as described on p. 1416, and the base produced condensed with an excess of phenanthraquinone in glacial acetic acid. The compound (1.3 g.) produced separates from anisole, in which it is very slightly soluble in the cold, in deep yellow prisms, m. p. 343° (corr.) (Found: Cl, 26.6.  $C_{21}H_{11}N_2Cl_3$  requires Cl, 26.8%), and may be 1 : 3 : 4-trichloro-2-methylbenzophenanthrazine, which would be the expected product if nuclear substitution had taken place in the chlorination. It is not easy, however, to understand why such a small quantity of it is formed, and why the chlorination does not proceed, as would be expected, to give 2 : 5 : 6-trichloro-4-nitrotoluene as the chief product. A pure substance could be obtained neither from the chlorination product nor from the nitration product of this by repeated crystallisation.

This phenanthrazine is different from that obtained from the highest-melting substance [after the removal of (V)] formed in the nitration of the dichlorination product of *p*-nitrotoluene. The lower-melting portions of this product, which almost certainly contains several 3 : 4-dinitrotoluene derivatives, were not examined from the point of view of the formation of phenanthrazine derivatives.

#### *Summary.*

The product of monochlorination of 2-chloro-4-nitrotoluene in presence of antimony trichloride, from which more than 30% of 2 : 6-dichloro-4-nitrotoluene had previously been isolated (J., 1922, 121, 806), has now been shown to contain, in addition to considerable quantities of substances other than nuclear-substituted dichloro-4-nitrotoluenes, 47.9% of that compound, estimated as 2 : 6-dichloro-3 : 4-dinitrotoluene. This result, when compared with the nitration of 2-chloro-4-nitrotoluene (Morgan and Drew, J., 1920, 117, 793), in which more than 85% of the product is 2-chloro-4 : 5-dinitrotoluene, shows that a change of substitution type has occurred.

The authors are indebted to the Victorian Government Research Grant Committee for a grant towards the cost of chemicals.

### CLXXXIV.—*The Boiling Points of Some Higher Aliphatic n-Hydrocarbons.*

By FRANCIS FRANCIS and NORMAN EDWARD WOOD.

THE long-continued fractionation of Scotch paraffin wax led to the isolation of seven fractions of constant boiling point (J., 1922, 121, 1529), and later (*loc. cit.*, p. 2804), evidence was advanced for the belief that these fractions were pure hydrocarbons. Piper and his students (J., 1925, 127, 2194) submitted these hydrocarbons to X-ray analysis, and finding that the spacings coincided with those obtained by Müller and Saville for synthetic hydrocarbons (*loc. cit.*, p. 600), concluded that "the hydrocarbons obtained from paraffin wax are identical in constitution with the synthetic *n*-hydrocarbons."

Certainly, then, as regards the material obtained from shale in Scotland fusing between 55° and 56°, and most probably paraffin from all sources, the view that has been held since Krafft's work in 1888 has been proved finally to be correct. The number of hydrocarbons present in different paraffins is still an open question, but if Scotch wax is at all typical, the number is not so large as Krafft stated, and is much nearer 10 to 12 than the 35 (18 of which were considered to be pure) that he believed to be present in the specimen he investigated (*Ber.*, 1907, 40, 4779).

In Piper's communication, the question was raised of the untrustworthiness of the molecular magnitudes of some of the hydrocarbons from paraffin wax as determined by the ordinary ebullioscopic methods.

We thought it most probable that a direct comparison of the boiling points of synthetic *n*-docosane,  $C_{22}H_{46}$ , with fraction B over a range of pressures would show either that these two substances were identical, which Piper states to be the case, or that B was  $C_{23}H_{48}$ , the deduction from a series of very concordant molecular-weight determinations by the ebullioscopic method. *n*-Docosane was synthesised by the electrolysis of a solution of potassium laurate "Kahlbaum" (Petersen, *Z. Elektrochem.*, 1906, 12, 141) and purified by three crystallisations from benzene; it fused at 44.5° and the specimen used for this work boiled at a constant temperature.

A boiling-point graph drawn from the data (Table I) for this synthetic material showed that all the boiling points at different pressures of the hydrocarbon B isolated from paraffin fell on that curve. There can therefore be no doubt that the two substances are identical, that one of the constituents of paraffin is

*n*-docosane, and that the molecular-weight determination of this hydrocarbon from that source was too high by about 4%.

TABLE I.

*Boiling points at various pressures (uncorr.).*

Fraction.							
B ( $C_{22}H_{46}$ ).		C ( $C_{24}H_{50}$ ).		E ( $C_{26}H_{54}$ ).		F ( $C_{28}H_{58}$ ).	
27.1 mm.	236°	27.6 mm.	255.5°	26.5 mm.	269°	28.0 mm.	288°
16.0	224	13.3	238.5	14.2	257	12.1	267.5
9.9	212	4.4	210.5	8.4	245.5	7.1	258.5
4.8	199.5	2.5	202	4.4	233	3.6	244
2.0	189	1.5	195	2.1	223.5		

Fraction.							
G ( $C_{29}H_{60}$ ).		C.O. ( $C_{24}H_{50}$ ).		F.O. ( $C_{28}H_{58}$ ).			
19.0 mm.	290.5°	24.6 mm.	253°	26 mm.	287°		
13.6	279.5	12.5	236.5	14.9	274.5		
8.3	270.5	7.3	221	7.1	258.5		
4.1	254	3.7	209	4.5	247		
2.5	248			2.2	234		

Synthetic Hydrocarbons.

$C_{16}H_{34}$ .		$C_{22}H_{46}$ .		$C_{30}H_{62}$ .		$C_{34}H_{70}$ .	
19.5 mm.	161.5°	24.7 mm.	233.5°	30.5 mm.	311.5°	30 mm.	337.5°
13.8	156	18.3	226	20.5	300	19.5	325
9.0	145	11.2	215	14.5	291	15.0	319
5.3	137	5.0	198	6.2	268	4.6	297.5
				1.7	241.5	2.4	285

The synthetic hydrocarbons ( $C_{24}$ ,  $C_{25}$ ,  $C_{26}$ ,  $C_{28}$ ,  $C_{29}$ ,  $C_{31}$ ) required to make a similar direct comparison between the other six hydrocarbons isolated from paraffin were not available.

Consequently we synthesised *n*-hexadecane, *n*-triacontane, and *n*-tetratriacontane in order to obtain the relationship between the boiling points at 15 mm. of these hydrocarbons and their respective carbon contents. This would enable a comparison to be made with the boiling points under the same pressure of the hydrocarbons isolated from paraffin.

Hexadecane was prepared by the reduction of cetyl iodide and purified by treatment with concentrated sulphuric acid; it showed a constant boiling point of 156°/13.8 mm. Triacontane and tetratriacontane were synthesised by the electrolysis of the potassium salts of palmitic and stearic acids, respectively, these acids being the purest obtainable from Kahlbaum. Each hydrocarbon was purified by three crystallisations from benzene and the specimens used in this investigation had constant boiling points.

From the data for the synthetic hydrocarbons in Table I, the boiling points at 15 mm. can be obtained by interpolation, and when these were plotted against their respective carbon contents a smooth curve resulted.

On this curve, within an experimental error of between  $1^{\circ}$  and  $2^{\circ}$ , lay the boiling points at 15 mm. of the following hydrocarbons isolated from paraffin:  $C_{24}H_{50}$ ,  $C_{26}H_{54}$ ,  $C_{28}H_{58}$ ,  $C_{29}H_{60}$ . We had insufficient amounts of the hydrocarbons  $C_{25}H_{52}$  and  $C_{31}H_{64}$  from paraffin to determine the boiling points with any degree of accuracy.

As these results are in entire agreement both with the molecular weights of these paraffin hydrocarbons as determined by the Menzies and Wright apparatus (J., 1925, 127, 2194) and with those obtained by X-ray analysis, there can be no doubt that the paraffin wax investigated in these laboratories contains in addition to *n*-docosane, the *n*-hydrocarbons tetracosane, hexacosane, octacosane, and nonacosane. The two (pentacosane and hentriacontane) whose boiling points at 15 mm. have not been determined had been analysed by X-rays and can clearly be added to this list.

It has been shown (J., 1922, 121, 2808) that on the oxidation of the seven hydrocarbons obtained from paraffin, in each case the small amounts which escaped this process were identical with the hydrocarbon used, and this fact was taken as a criterion that pure specimens had been isolated. Sufficient amounts of the unchanged hydrocarbons from the oxidation of tetracosane and octacosane (from paraffin) were available for the purpose of determining their boiling points at different pressures; in both cases these lay on the graphs for the parent hydrocarbons (see Table I, Fractions C.O. and F.O.). This constitutes a further proof of their identity and an additional support for the view that the two hydrocarbons are pure materials.

All the boiling points given in Table I were determined in an apparatus similar to that used for the fractionation of wax (J., 1922, 121, 1529), but the data obtained were not corrected for the exposed stem of the thermometer.

Krafft prepared a large number of synthetic *n*-hydrocarbons in 1882 and 1886 (*Ber.*, 15, 1687, 1711; 19, 2218), and we found that the boiling points at 15 mm. recorded by him for the ten hydrocarbons  $C_{15}H_{32}$  to  $C_{24}H_{50}$  fell on the graph (connecting b. p. and carbon content) constructed from our more limited data. Even in the case of  $C_{27}H_{56}$ ,  $C_{31}H_{64}$ ,  $C_{32}H_{66}$ , and  $C_{35}H_{72}$ , the difference was only  $+2^{\circ}$ .

This correspondence with our uncorrected data was so striking that we concluded that Krafft's boiling points at 15 mm. could not have been corrected for the exposed stem of the thermometer. It appeared to us that the corrections, certainly necessary for our own data, were equally applicable to his.

On the thermometer used in this work and with the same appa-

ratus the boiling point of naphthalene at 744.2 mm. was 211.1°, and of benzophenone 293.5° at 749 mm. Dimmer's formula for the correction (Landolt-Bornstein, ii, 1212) being applied, these data become 216.9° and 305.9° at 760 mm., which are in agreement with the recorded boiling points of these substances, *viz.*, 217.2° and 305.9°. The correction amounts to 1.7° at 150°, 4.5° at 200°, 8.3° at 250°, and 12.3° at 300°.

In Table II are the most probable corrected boiling points at 15 mm. of Krafft's hydrocarbons and those described in this communication; the error, we believe, does not exceed  $\pm 1.5^\circ$ .

TABLE II.

*Boiling points of n-hydrocarbons (corrected) at 15 mm.;  
probable accuracy  $\pm 1.5^\circ$ .*

C <sub>15</sub> H <sub>32</sub>	Synthetic K	144°	C <sub>25</sub> H <sub>52</sub>	Interpolated	259°
C <sub>16</sub> H <sub>34</sub>	" K, F	158	C <sub>26</sub> H <sub>54</sub>	Paraffin F	268
C <sub>17</sub> H <sub>36</sub>	" K	171	C <sub>27</sub> H <sub>56</sub>	Synthetic K	277
C <sub>18</sub> H <sub>38</sub>	" K	184	C <sub>28</sub> H <sub>58</sub>	Paraffin F	286
C <sub>19</sub> H <sub>40</sub>	" K	196	C <sub>29</sub> H <sub>60</sub>	" F	295
C <sub>20</sub> H <sub>42</sub>	" K	208	C <sub>30</sub> H <sub>62</sub>	Synthetic F	304
C <sub>21</sub> H <sub>44</sub>	" K	219	C <sub>31</sub> H <sub>64</sub>	" K	312
C <sub>22</sub> H <sub>46</sub>	" K, F	230	C <sub>32</sub> H <sub>66</sub>	" K	320
	and paraffin		C <sub>33</sub> H <sub>68</sub>	Interpolated	328
C <sub>23</sub> H <sub>48</sub>	" K	240	C <sub>34</sub> H <sub>70</sub>	Synthetic F	336
C <sub>24</sub> H <sub>50</sub>	" K, F	250	C <sub>35</sub> H <sub>72</sub>	" K	344
	and paraffin				

K = Krafft.

F = present communication.

The observed b. p. of our specimen of hexadecane on the thermometer used in this investigation was 278° at 764.8 mm.; correction for exposed stem raises this to 288.6°. Within the experimental error, this agrees with Krafft's determination, *viz.*, 287.5° at 760 mm.

Since the boiling point at 760 mm. recorded by Krafft for this hydrocarbon, and also those of C<sub>17</sub>H<sub>36</sub>, C<sub>18</sub>H<sub>38</sub>, and C<sub>19</sub>H<sub>40</sub>, all lie on a smooth curve connecting boiling points and carbon content, there can be no doubt that, as far as these hydrocarbons are concerned, Krafft's data at normal pressure were corrected for the exposed stem of the thermometer.

Our warmest thanks are due to Professor Sydney Young of Trinity College, Dublin, for the great assistance he has given us in considering and comparing our results with those of Krafft. In Krafft's communications to the *Berichte* there are many cases in which it is not possible to be certain whether the data recorded have or have not been corrected in the manner discussed in this communication.

CLXXXV.—*The Monochloro-derivatives of m-Cresol.*

By GEORGE PHILIP GIBSON.

EXCEPT in the case of 6-chloro-*m*-cresol (Kalle and Co., D.R.-PP. 90,847 and 93,694; Friedländer's "Fortschritte," Vol. IV, 94) and 6-chloro-*m*-methoxybenzoic acid (Peratoner and Condorelli, *Gazzetta*, 1898, 28, i, 214), little information is given in the literature regarding the monochloro-derivatives of *m*-cresol (Mazzura, *Gazzetta*, 1899, 29, i, 380; 1900, 30, ii, 84; Friedländer and Schenk, *Ber.*, 1914, 47, 3040; Raschig, D.R.-P. 232,071, 1909; Biechele, *Annalen*, 1869, 151, 115).

The author has studied the monochlorination of *m*-cresol, isolated the 2-, 4-, and 6-chloro-*m*-cresols (the first with difficulty), and converted them into the corresponding chloro-*m*-methoxybenzoic acids. The constitutions of these were determined by preparing the respective compounds from the corresponding 2-, 4-, and 6-nitro-*m*-cresols (Gibson, J., 1923, 123, 1267) by successive methylation, reduction, substitution of chlorine for the amino-group, and oxidation of the resulting chloro-*m*-tolyl methyl ethers.

The reduction of 2-nitro-*m*-tolyl methyl ether by tin and hydrochloric acid produces an oily mixture of bases instead of the pure 3-methoxy-*o*-toluidine which is formed when iron and dilute acetic acid are used (Gibson, *loc. cit.*). The least volatile constituent of this mixture is a chloro-base, m. p. 47°. This is probably 5-chloro-3-methoxy-*o*-toluidine, since an isomeric base, m. p. 50°, was obtained by reducing 6-chloro-2-nitro-*m*-tolyl methyl ether.

## EXPERIMENTAL.

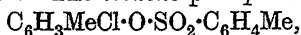
*Chlorination of m-Cresol.*—A saturated solution of chlorine (1.1 mols.) in carbon tetrachloride (7.5 g. in 100 c.c.) was added gradually to a mechanically stirred solution of *m*-cresol in carbon tetrachloride. The solvent was then evaporated and the residue fractionally distilled. After five operations, 37% of the product boiled at 196–197° and 47% at 231–233°.

The fraction, b. p. 196–197°, was seeded at 0° with a crystal of 4-chloro-*m*-cresol obtained by the hydrolysis of 4-chloro-*m*-tolyl toluene-*p*-sulphonate. The crystals thus produced were separated from the residual oil, washed quickly with ice-cold light petroleum, and recrystallised from that solvent. The crystals obtained by seeding the residual oil, diluted with an equal volume of light petroleum (b. p. 50–60°), at –15° were similarly treated.

4-Chloro-*m*-cresol was thus obtained (29% of the fraction) in large, colourless prisms, m. p. 46°, b. p. 196° (Found: Cl, 24.8.



$C_7H_7OCl$  requires Cl, 24.8%). The *methyl ether* is a colourless, pleasant-smelling liquid, b. p. 212.5°. The *acetate* has b. p. 122—123°/11 mm. The *benzoate* separates from alcohol in massive tablets containing alcohol, m. p. 31°, and from light petroleum in crystals, m. p. 40°. The *toluene-p-sulphonate*,



crystallises from alcohol or acetone in large, six-sided prisms, m. p. 96°. It is sparingly soluble in alcohol or light petroleum.

The mixture of chloro-*m*-cresols obtained from the final petroleum mother-liquor (p. 1424) was converted almost quantitatively by treatment with sodium hydroxide solution and methyl sulphate into a mixture of ethers, b. p. 218—219°, which on oxidation with boiling dilute permanganate solution gave a theoretical yield of a mixture, m. p. 185—196°, of chloromethoxybenzoic acids. This mixture, systematically crystallised from chloroform, gave 42% of 4-chloro-*m*-methoxybenzoic acid, m. p. 211°. The final mother-liquors yielded a glue-like mass, which was dissolved in ether and fractionally extracted with 1% aqueous sodium hydroxide; the ethereal solution of the acid from each of these fractions was again extracted with an aqueous solution of the sodium salt of the next fraction. By repeated treatment of this kind, the mixture was completely separated into 2-chloro- and 4-chloro-*m*-methoxybenzoic acids.

2-Chloro-*m*-cresol, the presence of which in the crude chlorination product was thus established, was obtained by boiling its methyl ether (below) with hydriodic acid for 6 hours. The product was freed from the unchanged methyl ether with the aid of sodium hydroxide and distilled (b. p. about 194°); it then crystallised from light petroleum in massive, ill-defined, transparent crystals, m. p. 55—56°, having a pronounced phenolic odour and being very sparingly soluble in cold water. The *methyl ether*, prepared from 2-nitro-*m*-tolyl methyl ether (p. 1426), crystallised from light petroleum in massive prisms, m. p. 24.2°, b. p. 218.5° (Found : Cl, 22.7.  $C_8H_9OCl$  requires Cl, 22.7%).

6-Chloro-*m*-cresol.—A portion (49%) of the fraction of the crude chlorination product, b. p. 231—233°, solidified, and recrystallisation from light petroleum gave pure 6-chloro-*m*-cresol, m. p. 57° (Kalle and Co., *loc. cit.*, give 66°), b. p. 234° (Found : Cl, 24.9. Calc. : Cl, 24.8%).

The *methyl ether* boils at 213.5° and the *acetate* at 123—124°/11 mm. The *benzoate*, m. p. 86°, crystallises in thin, rectangular plates from alcohol, carbon tetrachloride, or light petroleum, and is not freely soluble in the latter two (Found : C, 68.1; H, 4.5.  $C_{14}H_{11}O_2Cl$  requires C, 68.2; H, 4.4%). The *toluene-p-sulphonate*,

m. p. 98°, crystallises from alcohol and light petroleum, in both of which it is only slightly soluble, in plates and needles respectively.

The mother-liquors from the 6-chloro-*m*-cresol (p. 1425) gave, on evaporation, a solid of low melting point, which was treated with methyl sulphate and alkali; the resulting mixture of methyl ethers\* gave, after repeated fractional distillation, 35% of 6-chloro-*m*-tolyl methyl ether (b. p. 213.5°) and about 21% of a liquid, b. p. 248–249°, which was probably a mixture of 2:6- and 4:6-dichloro-*m*-tolyl methyl ethers.

*Reduction of 2-Nitro-m-tolyl Methyl Ether* (compare Gibson, J., 1923, 123, 1267; Hodgson and Beard, J., 1925, 127, 498).—By the action of tin and hydrochloric acid on this ether a mixture (m. p. 27°) of 3-methoxy-*o*-toluidine and 5-chloro-3-methoxy-*o*-toluidine (about 10% of the product) is produced. The former is removed by fractional distillation in steam, and the residue, after being freed from a red impurity by distillation in a vacuum, separates from light petroleum in slender needles of 5-chloro-3-methoxy-*o*-toluidine, m. p. 47°, b. p. 140–142°/11.5 mm., which are slightly soluble in light petroleum (Found: N, 8.1.  $C_8H_{10}ONCl$  requires N, 8.2%).

The *acetyl* derivative, obtained by means of acetic anhydride containing a trace of sulphuric acid (Smith and Orton, J., 1908, 93, 1250), crystallises from alcohol, acetone, or benzene in colourless needles, m. p. 170°. It is sparingly soluble in water, light petroleum, carbon tetrachloride, or benzene (Found: N, 6.5.  $C_{10}H_{12}O_2NCl$  requires N, 6.6%).

*2-Chloro-m-tolyl Methyl Ether*.—The more volatile portion of the steam distillate (see above), consisting of 3-methoxy-*o*-toluidine with a small proportion of the chloro-base just described, is transformed into a mixture of chloro- and dichloro-*m*-tolyl methyl ethers by the Sandmeyer method. This product is distilled in steam, extracted from the distillate with ether, freed from any phenolic compounds by shaking with dilute aqueous alkali hydroxide, and repeatedly fractionally distilled. 2-Chloro-*m*-tolyl methyl ether (p. 1425) is thus obtained in a pure state (yield 54%, calculated on the nitro-compound used). The fractions of high boiling point, after distillation in a vacuum and recrystallisation from light petroleum, give 2:5-dichloro-*m*-tolyl methyl ether (yield 8.7%), which crystallises from light petroleum in slender

\* Methylation in this type of compound overcomes the lowering of the boiling point due to the ortho Cl:OH grouping and the effect of a second chlorine atom in the molecule is then appreciable: 6-chloro-*m*-tolyl methyl ether boils at 213.5° and 4:6-dichloro-*m*-tolyl methyl ether at 249°, whereas the corresponding cresols boil at 234° and 232°, respectively.

prisms, m. p. 52°, b. p. 119—120°/12.5 mm., having the pleasant odour characteristic of these chloro-ethers (Found : OMe, 16.2; Cl, 37.0.  $C_8H_8OCl_2$  requires OMe, 16.2; Cl, 37.1%).

6-Chloro-2-nitro-*m*-tolyl methyl ether is formed when 2-nitro-*m*-tolyl methyl ether is treated with chlorine at 160—170° until the gain in weight corresponds to 1 g.-atom. The dark reddish-brown product is repeatedly distilled (10 mm.) to free it from unchanged 2-nitro-ether (b. p. 120—130°), and the larger fraction (b. p. 140—145°), which solidifies, is fractionally crystallised from alcohol in order to remove some impurity, probably 4-chloro-2-nitro-*m*-tolyl methyl ether, which crystallises from the mother-liquors in tufts of very slender needles.

The 6-chloro-derivative (yield 55%) crystallises readily from alcohol, light petroleum, or carbon tetrachloride in large, pale yellow prisms, m. p. 112°. It is sparingly soluble in hot or cold water, alcohol, light petroleum, or carbon tetrachloride, but is fairly easily soluble in acetone, benzene, or chloroform (Found : Cl, 17.9.  $C_8H_8O_3NCl$  requires Cl, 17.65%).

6-Chloro-3-methoxy-*o*-toluidine, prepared by reducing the preceding compound with iron borings and dilute acetic acid (compare p. 1424), crystallises from light petroleum, in which it is fairly easily soluble, in long needles, m. p. 50°, b. p. 145—146°/12 mm. (Found : N, 8.2.  $C_8H_{10}ONCl$  requires N, 8.2%).

The acetyl derivative, m. p. 154°, crystallises readily from organic solvents, and is sparingly soluble in light petroleum, carbon tetrachloride, or benzene (Found : N, 6.3.  $C_{10}H_{12}O_2NCl$  requires N, 6.6%).

When diazotised 6-chloro-3-methoxy-*o*-toluidine is treated with an alkaline solution of sodium stannite, and the resulting 6-chloro-*m*-tolyl methyl ether (b. p. 213—214°) oxidised with boiling dilute permanganate solution, 6-chloro-*m*-methoxybenzoic acid, m. p. 173.5°, is obtained (p. 1428).

*Orientation of the 2-, 4-, and 6-Chloro-m-cresols.*—The orientation of 2-chloro-*m*-cresol, by the preparation of its methyl ether from 2-nitro-*m*-cresol, has already been described (p. 1426). From the isomeric 4- and 6-nitro-*m*-cresols, the corresponding chloro-*m*-tolyl methyl ethers were prepared in a similar manner and oxidised to the corresponding chloro-*m*-methoxybenzoic acids. These compounds were identical respectively with those prepared by methylating the 4- and 6-chloro-*m*-cresols and oxidising the methyl ethers to the corresponding chloro-acids. These results are confirmed by the observed differences in the rates of oxidation of the methyl ethers to the acids; comparative experiments showed that the times required for the oxidation of equal weights (5 g.) of the

ethers were: 2-chloro-, 7.25 hours; 4-chloro-, 2.7 hours; and 6-chloro-, 6.7 hours.

2-Chloro-*m*-methoxybenzoic acid,\* m. p. 160.5°, is almost insoluble in benzene, chloroform, carbon tetrachloride, or light petroleum (b. p. 60–80°) (Found: equiv., 186.9. Calc. for  $C_8H_7O_3Cl$ : equiv., 186.5). 4-Chloro-*m*-methoxybenzoic acid,\* m. p. 211°, crystallises from 50% aqueous alcohol in slender prisms and from chloroform in plates (Found: equiv., 186.5). 6-Chloro-*m*-methoxybenzoic acid, m. p. 173.5° (Peratoner and Condorelli, *loc. cit.*, give 171°), is only sparingly soluble in benzene, light petroleum, or carbon tetrachloride, but dissolves freely in alcohol, acetone, or chloroform (Found: equiv., 187.6).

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## CLXXXVI.—*The Action of Thionyl Chloride on Hydroxyanthraquinones. Part II. Quinizarin.*

By ALBERT GREEN.

THE action of quinizarin on boiling thionyl chloride is different from that of alizarin (J., 1924, 125, 1450). One hydroxyl group of quinizarin is replaced by a chlorine atom, which is reactive, and the product consists of deep red needles. In these and other properties the compound differs from the known monochloro-monohydroxyanthraquinones.

Slight loss of chlorine (1–2%) occurs when the compound is heated at 100°, or is boiled with acetic acid, for 1 hour. When a solution in concentrated sulphuric acid is heated on the boiling water-bath, the chlorine is eliminated as hydrogen chloride, and after 1 hour quinizarin is obtained in quantitative yield. The same product results from treatment with aqueous alkalis, and also by heating the *chloro*-compound under pressure with absolute methyl or ethyl alcohol or with acetic acid.

Oxidation with alkaline permanganate yields phthalic acid.

When a solution of the chloro-compound in absolute alcohol containing 3% of hydrogen chloride is heated, a product is obtained

\* Since this paper was written, these acids have been prepared by Hodgson (*this vol.*, p. 150).

which is isomeric with the known monoethyl ether of quinizarin (Liebermann and Jellinek, *Ber.*, 1888, **21**, 1168). This product is converted into quinizarin by heating it with concentrated sulphuric acid at 100° for an hour.

Treatment of the chloro-compound with boiling acetic anhydride, alone or with concentrated sulphuric acid, converts it into diacetyl derivatives of quinizarin. Efforts to isolate a monoacetyl derivative were fruitless, as in all cases some decomposition occurred with loss of chlorine. Similarly the products of methylation with diazomethane were not uniform and contained varying amounts of chlorine, although the analyses pointed to the presence of one methoxyl group only.

The chloro-compound condenses rapidly with boiling aniline and *p*-toluidine with loss of hydrogen chloride and production of *monoaminomonohydroxy*-compounds; longer treatment in presence of boric acid gives *diaminoanthraquinones*. These derivatives are respectively isomeric with the mono- and di-amino-compounds obtained by the condensation of quinizarin with aromatic amines, and the different colours of the solutions in concentrated sulphuric acid afford a means of distinguishing the isomerides.

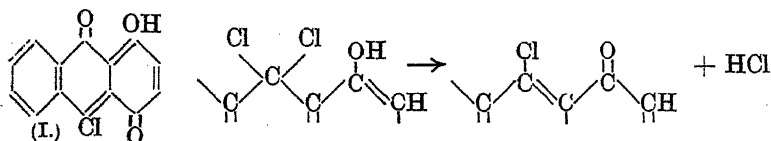
While the replacement of one hydroxyl group of quinizarin by chlorine would be expected to give 1-chloro-4-hydroxyanthraquinone, it is obvious that the properties of the compound under consideration are not consonant with those of a chlorohydroxyanthraquinone in which the halogen is in one of the outer rings. 1-Chloro-4-hydroxyanthraquinone separates from alcohol in golden-yellow needles melting at 193°. It is unaffected by heating its solution in concentrated sulphuric acid for 1 hour at 100°, and is converted into quinizarin only when it is heated for several hours at 140° with sulphuric and boric acids (Eckert and Steiner, *Monatsh.*, 1914, **35**, 1145).

The replacement of a hydroxyl group by a chlorine atom by means of thionyl chloride connotes an acidic hydroxyl, and this is a well-known method of preparing the acid chlorides of carboxylic acids. Properties similar to those of an acid chloride are shown by this new derivative of quinizarin; such are its rapid condensation with amines, and the tendency of the chlorine atom to react with diazomethane. The interaction of what may be called "normal" chloroanthraquinones with amines is slow even in the presence of catalysts (compare, among others, Harrop, Norris, and Weizmann, *J.*, 1909, **95**, 1313). Meyer and Sander (*Annalen*, 1912, **396**, 145), however, have shown that halogen-substituted anthrones, in which the halogen atom is attached to a *meso*-carbon atom, react readily with amines, giving aminoanthrones.

The only structure which appears to account adequately for the properties of the new compound is that of 10-chloro-1-hydroxy-4:9-anthraquinone (I). This formula necessitates an ortho-quinonoid grouping, and in this connexion the deep red colour of the compound is noteworthy, and is not found in "normal" mono-hydroxy-9:10-anthraquinones, which are yellow.

Probably 10-chloro-1-hydroxy-4:9-anthraquinone is formed from quinizarin in one of two ways. (1) Quinizarin may exist in a reactive ortho-quinonoid state in which the two hydroxyl groups are in the 1:10 positions instead of the 1:4 as usually formulated.  $\alpha$ -Hydroxyl groups of hydroxyanthraquinones react with methylating and acylating agents much less rapidly than similar groups in  $\beta$ -positions. This fact and others have given rise to suggestions both of co-ordination between the hydrogen atoms of the  $\alpha$ -hydroxyls and the neighbouring carboxyl oxygen atoms (Dimroth and Faust, *Ber.*, 1921, **54**, 3020; Sidgwick and Callow, *J.*, 1924, **125**, 527), and also of isomeric structures in which the hydrogens of the  $\alpha$ -hydroxyl groups are attached to the *meso*-oxygen atoms (Perkin, *J.*, 1899, **75**, 453; Georgievics, *Monatsh.*, 1911, **32**, 329), to give ortho-quinonoid formulæ. There is, however, no recorded instance of a hydroxy-9:10-anthraquinone reacting in such an isomeric form.

(2) The reaction may occur in two stages. The first stage may be represented by the replacement of a carbonyl oxygen atom by two chlorine atoms—a reaction of this type occurs between benzaldehyde and thionyl chloride to give benzal chloride (Loth and Michaelis, *Ber.*, 1894, **27**, 2548). The second stage would then consist of the union of one of these chlorine atoms and the



hydrogen atom of the neighbouring hydroxyl group, giving hydrogen chloride and 10-chloro-1-hydroxy-4:9-anthraquinone. It is intended to test this theory of the mechanism of the reaction by an examination of the action of thionyl chloride on the ethers of quinizarin.

Both the above interpretations leave unexplained why only one of the carbonyl groups of quinizarin appears to take part in the reaction.

In the preparation of pure quinizarin for this investigation it was observed that the diacetyl derivative exists in two polymorphic forms with different melting points.

## EXPERIMENTAL.

*Quinizarin*.—Pure diacetylquinizarin (see p. 1435) was heated with concentrated sulphuric acid (6 parts) at 100° for 30 minutes, and the solution was then stirred into cold water. After boiling for 10 minutes, the mixture was filtered, the quinizarin washed with boiling water until free from acid, and dried at 100°. It assumed a dark metallic lustre at 183° and melted at 197–198°.

10-*Chloro-1-hydroxy-4:9-anthraquinone*.—When 30 g. of quinizarin were boiled with 120 c.c. of recently distilled thionyl chloride, solution occurred rapidly with evolution of sulphur dioxide and hydrogen chloride. After 8–30 hours, the deep red liquid was concentrated to half bulk. On cooling in a dry atmosphere, it deposited dark red, fine needles (26 g.), m. p. 225–226° (even after recrystallisation from methyl or ethyl alcohol or benzene); a further 4 g. were obtained by concentrating the filtrate. The product was washed free from thionyl chloride with dry benzene and ether and dried in a vacuum over fused calcium chloride and soda lime (Found: C, 65.0; H, 2.8; Cl, 13.7; *M*, cryoscopic in naphthalene, 265, 260.  $C_{14}H_7O_3Cl$  requires C, 65.0; H, 2.7; Cl, 13.7%; *M*, 258.5). It gave a bright red colour with alcoholic ferric chloride and when warmed with pyridine formed a dirty brown solution which slowly deposited a black, apparently amorphous powder.

A mixture of 40 c.c. of 10% aqueous potassium hydroxide, 2 g. of the quinone, and 100 c.c. of 10% potassium permanganate solution was boiled for 2 hours, and the excess of permanganate destroyed by alcohol; from the colourless acidified filtrate ether extracted 0.8 g. of impure phthalic acid (identified in the form of the anhydride, from which fluorescein was prepared).

*Conversion into quinizarin*. (1) *By sulphuric acid*. A solution (reddish-purple) of 0.86 g. of 10-chloro-1-hydroxy-4:9-anthraquinone in 20 c.c. of concentrated sulphuric acid was heated on a boiling water-bath for 1 hour and then poured into water, the suspension boiled, and the light red precipitate (0.79 g., theoretical) collected and dried (Found: C, 69.8; H, 3.3. Calc.; C, 70.0; H, 3.3%). It melted at 197° alone and when mixed with pure quinizarin, and when acetylated in pyridine gave a diacetyl derivative in prisms, m. p. 206–208°.

(2) *By acetic acid*. A mixture of 0.9 g. of the quinone and 2 c.c. of acetic acid was heated, with or without 0.3 g. of freshly-fused potassium acetate, in a sealed tube for 3 hours at 180°. The product, on recrystallisation from 20 c.c. of boiling acetic acid (bone charcoal), gave 0.3–0.4 g. of red needles which, alone or

mixed with pure quinizarin, melted at  $197^{\circ}$  (Found: C, 69.8; H, 3.4%).

(3) *By methyl alcohol.* When 0.85 g. of the quinone was heated in a sealed tube at  $200^{\circ}$  for 2 hours with 2 c.c. of absolute methyl alcohol, and the product recrystallised from methyl alcohol (bone charcoal), 0.4 g. of quinizarin, m. p.  $196-197^{\circ}$ , was obtained (Found: C, 70.0; H, 3.4%).

(4) *By ethyl alcohol.* When the experiment was repeated with absolute ethyl alcohol, 0.3 g. of quinizarin was obtained (Found: C, 69.7; H, 3.3%).

(5) *By sodium or potassium hydroxide.* A paste of the quinone (3 g.) and an excess of concentrated aqueous sodium or potassium hydroxide was boiled with water for 5 minutes and stirred into an excess of boiling dilute hydrochloric acid. The reddish-brown solid (2.5 g.) produced crystallised from acetic acid in red needles of quinizarin, m. p.  $195-197^{\circ}$  (alone and mixed) (Found: C, 69.7; H, 3.3%), which was converted into its diacetyl derivative, m. p.  $206-208^{\circ}$ .

*Acetylation.* (1) *Acetic anhydride alone.* 10-Chloro-1-hydroxy-4:9-anthraquinone (4 g.) was boiled with 40 c.c. of acetic anhydride until fumes of hydrogen chloride (due to decomposition, by atmospheric moisture at the top of the condenser, of acetyl chloride produced in the reaction) were no longer observed (4 hours). The original dark red colour became dark green, and from the filtered, cooled solution small, olive-green crystals (4.2 g.), m. p.  $204^{\circ}$ , separated. These were repeatedly crystallised from acetic anhydride (bone charcoal) and finally twice from pyridine; the characteristic yellow prisms of diacetylquinizarin were then obtained which, alone or mixed with an authentic specimen, melted at  $207-208^{\circ}$ . A quantitative experiment showed that the substance did not contain chlorine [Found: C, 66.7; H, 3.6;  $\text{CH}_3\cdot\text{CO}$ , 26.7; *M*, in freezing naphthalene, 310, 315. Calc. for  $\text{C}_{14}\text{H}_6\text{O}_4(\text{CO}\cdot\text{CH}_3)_2$ : C, 66.7; H, 3.7;  $\text{CH}_3\cdot\text{CO}$ , 26.7%; *M*, 324].

Hydrolysis of this acetyl derivative by an alcoholic solution of sulphuric acid yielded quinizarin, m. p.  $198^{\circ}$  (Found: C, 69.9; H, 3.3%).

(2) *Acetic anhydride and sulphuric acid.* When 2.2 g. of 10-chloro-1-hydroxy-4:9-anthraquinone were heated to boiling with 10 c.c. of acetic anhydride containing 2 drops of concentrated sulphuric acid, the red solution rapidly became yellow-green. The filtered solution slowly deposited 1.4 g. of very fine, pale yellow rods identical with those obtained by acetylating quinizarin under similar conditions (see under). The product of one recrystallisation from acetic anhydride containing sulphuric acid changed colour from yellow to light orange at about  $120^{\circ}$  and melted at  $200-201^{\circ}$



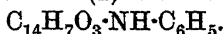
(Found: C, 66.5; H, 3.8;  $\text{CH}_3\text{-CO}$ , 26.6%). This diacetyl derivative separated from pyridine in small, yellow prisms, m. p. 207—208°.

Numerous experiments were carried out with a view to acetylating the single hydroxyl group. The chloro-compound was heated with acetyl chloride and potassium acetate under ordinary pressure, in benzene solution, and in sealed tubes at 90—100°. The products, however, were mixtures containing in some cases as little as 4% of chlorine. Attempted acetylations in pyridine with one molecular proportion of acetic anhydride yielded black amorphous products which would not crystallise and in which the chlorine content also varied.

*Methylation of 10-chloro-1-hydroxy-4:9-anthraquinone.* Since methylation in alkaline media was impossible, diazomethane was used. In every experiment chlorine was lost (4% in one experiment), and the products were not uniform. Nevertheless analyses clearly indicated the presence of one hydroxyl group.

In a typical experiment a suspension of 1.0 g. of the finely powdered dry compound in 30 c.c. of absolute ether at 5° was treated with an excess of diazomethane (from 2 g. of nitrosomethylurethane and 6 c.c. of 70% aqueous potassium hydroxide) in 60 c.c. of dry ether during  $\frac{1}{2}$  hour. Stirring was continued for 3 hours, and the red product (1 g.) collected after 12 hours. After darkening at about 190°, it melted to a black paste between 270° and 280° (Found: Cl, 12.1; OMe, 11.1.  $\text{C}_{14}\text{H}_6\text{O}_2\text{-OMe}$  requires Cl, 13.0; OMe, 11.4%).

*Condensations with amines.* (1) *Anilino-derivative,*



A solution of 1.5 g. of 10-chloro-1-hydroxy-4:9-anthraquinone in 8 c.c. of freshly distilled aniline was boiled for 5 minutes, the red colour changing to brown. The hot solution was stirred into an excess of dilute hydrochloric acid and boiled. The black precipitate was filtered off hot, washed free from acid and dried (1.9 g.). It separated from tetrachloroethane in black, microscopic crystals after the addition of a little ether. The product, which contained no chlorine, formed a paste at 272—274° and decomposed at 290°. It dissolved in concentrated sulphuric acid with a deep amethyst colour and in boiling sodium hydroxide to a very pale purple solution (Found: N, 4.3.  $\text{C}_{20}\text{H}_{13}\text{O}_3\text{N}$  requires N, 4.4%).

(2) *Dianilino-derivative,*  $\text{C}_{14}\text{H}_6\text{O}_2(\text{NH}\cdot\text{C}_6\text{H}_5)_2$ . A mixture of 1 g. of the chloro-compound, 0.5 g. of boric acid (dried at 120° for 4 hours), and 10 c.c. of freshly-distilled aniline was boiled for 6 hours, the purple colour becoming dark brown. It was stirred while hot into an excess of dilute hydrochloric acid, and the pre-

precipitate treated as in the previous experiment. The product consisted of black crystals (1.6 g.) which did not melt below  $310^{\circ}$ . It gave a golden-brown solution in concentrated sulphuric acid, but was insoluble in hot aqueous caustic soda (Found: N, 7.2.  $C_{26}H_{18}O_2N_2$  requires N, 7.2%).

The dianilino-derivative from quinizarin, prepared similarly, formed blue-black crystals from tetrachloroethane. These dissolved in sulphuric acid to a blue-black solution and were insoluble in boiling caustic soda solution (Found: N, 7.1%).

(3) *Mono-p-toluidino-derivative*,  $C_{14}H_7O_3 \cdot NH \cdot C_6H_4Me$ . This was prepared in a similar manner to the monoanilino-derivative. The product, which was free from chlorine (Carius), crystallised from acetic acid in microscopic, very dark brown needles which softened at  $280^{\circ}$  and showed no further change up to  $310^{\circ}$ . Its solution in sulphuric acid was amethyst and in caustic soda light purple (Found: N, 4.1.  $C_{21}H_{15}O_3N$  requires N, 4.3%).

The mono-*p*-toluidino-derivative\* from quinizarin melted at  $190-192^{\circ}$ , and dissolved in concentrated sulphuric acid with a brilliant green colour (Found: N, 4.2%).

(4) *Di-p-toluidino-derivative*,  $C_{14}H_6O_2(NH \cdot C_6H_4Me)_2$ . This was prepared similarly to (2) above, and crystallised from alcohol in bluish-black, microscopic needles which decomposed at  $305^{\circ}$  with previous sintering. The solution in sulphuric acid was dark honey-coloured (Found: N, 6.7.  $C_{28}H_{22}O_2N$  requires N, 6.7%).

The isomeric compound prepared from quinizarin gave a blue-black solution in concentrated sulphuric acid (Found: N, 6.8%).

10-*Ethoxy-1-hydroxy-4:9-anthraquinone*.—10-Chloro-1-hydroxy-4:9-anthraquinone (2.5 g.) was boiled with absolute ethyl alcohol (200 g.) containing 3% of dry hydrogen chloride for  $3\frac{1}{2}$  hours, the red solution becoming dark green and fluorescent. From the filtered, concentrated, cooled solution clusters of reddish-brown needles separated (2.1 g.), m. p.  $135^{\circ}$ , after recrystallisation from ethyl alcohol (Found: C, 71.3; H, 4.3; OEt, 16.3.  $C_{14}H_7O_3 \cdot OEt$  requires C, 71.6; H, 4.5; OEt, 16.9%).

This ether was very soluble in cold benzene and less soluble in cold ethyl alcohol. In concentrated sulphuric acid, its solution was similar to that given by quinizarin. When this solution was heated at  $100^{\circ}$  for 1 hour and then stirred into water, quinizarin (m. p.  $195-197^{\circ}$ ) was obtained in quantitative yield (Found: C, 70.0; H, 3.4%).

1-*Chloro-4-acetoxyanthraquinone*.—Commercial 1-chloro-4-hydroxyanthraquinone† was boiled with an excess of acetic anhydride

\* Kindly presented by the British Alizarine Co., Ltd., Manchester.

† Kindly presented by the Scottish Dyes, Ltd., Carlisle.

and a few drops of pyridine for  $\frac{1}{2}$  hour. The crude acetyl derivative was repeatedly crystallised from pyridine containing a little anhydride, until the melting point remained constant at 176—177°, the pure 1-chloro-4-acetoxyanthraquinone forming fine, pale primrose needles (Found: Cl, 11.8;  $\text{CH}_3\cdot\text{CO}$ , 14.4.  $\text{C}_{14}\text{H}_6\text{O}_3\text{Cl}\cdot\text{CO}\cdot\text{CH}_3$  requires Cl, 11.8;  $\text{CH}_3\cdot\text{CO}$ , 14.3%).

1-Chloro-4-hydroxyanthraquinone.—The pure acetyl derivative (2 g.) was hydrolysed by boiling for 2 hours with 140 c.c. of absolute alcohol containing 3 c.c. of concentrated sulphuric acid. On cooling, the hydroxy-compound separated in golden-yellow needles, m. p. 192—193°, unchanged by further recrystallisation (Found: Cl, 13.8. Calc. for  $\text{C}_{14}\text{H}_7\text{O}_3\text{Cl}$ : Cl, 13.7%). The alcoholic solution of 1-chloro-4-hydroxyanthraquinone gave a pale red colour with ferric chloride.

*Treatment of 1-Chloro-4-hydroxyanthraquinone with Sulphuric Acid.*—A solution of 3 g. in 50 c.c. of concentrated sulphuric acid was heated at 100° for 1 hour. The hot liquid was then stirred into 200 c.c. of cold water, the mixture boiled for 10 minutes, and the yellow product filtered off, washed with boiling water until acid-free, and dried at 100° (2.8 g.). The substance melted at 192°, alone and when mixed with an authentic specimen of 1-chloro-4-hydroxyanthraquinone (Found: Cl, 13.7%).

*Diacetylquinizarin.*—Liebermann and Giesel (*Ber.*, 1875, 8, 1648) describe diacetylquinizarin as "gelbe Saulchen" melting at 200°.

Quinizarin supplied by the British Dyestuffs Corporation, Ltd., was acetylated by boiling for 15 minutes with acetic anhydride containing a few drops of concentrated sulphuric acid. The product on purification was obtained in two polymorphic forms:

*Form A.* (1) Small, twinned, six-sided, yellow prisms from quickly chilled solutions in hot pyridine [Found: C, 66.6; H, 3.7;  $\text{CH}_3\cdot\text{CO}$ , 26.8; *M*, cryoscopic in naphthalene, 325.

$\text{C}_{14}\text{H}_6\text{O}_4(\text{CO}\cdot\text{CH}_3)_2$  requires C, 66.7; H, 3.7;  $\text{CH}_3\cdot\text{CO}$ , 26.7%; *M*, 324]. (2) Long, flat, six-sided, yellow plates by recrystallisation from acetic anhydride alone (Found: C, 66.4; H, 3.6;  $\text{CH}_3\cdot\text{CO}$ , 26.6%; *M*, 330). (3) Very thin, pale yellow needles from alcohol (Found: C, 66.7; H, 3.6;  $\text{CH}_3\cdot\text{CO}$ , 26.9%; *M*, 26.9). All three forms melted at 207—208°.

*Form B.* Sheaves of yellow needles or fine rods, which became light orange at about 120° and melted at 200—201° (Found: C, 66.6; H, 3.6;  $\text{CH}_3\cdot\text{CO}$ , 26.2%; *M*, 320). This form was converted into A by recrystallisation from pyridine, acetic anhydride, or alcohol, and hot solutions of A in acetic anhydride containing a few drops of sulphuric acid always deposited crystals of B only.

*Solubility Determinations.*—The two forms of the diacetyl derivative have identical solubilities in benzene and in chloroform at 25°. This may be accounted for by the long time required for saturation. Benzene, for example, was still unsaturated with respect to A after 15 hours' shaking at 25°.

In Table I the figures represent g. of solute per 100 g. of solution.

TABLE I.

Sub- stance.	Benzene.				Chloroform.			
	20 hrs.	30 hrs.	55 hrs.	Mean.	40 hrs.	55 hrs.	65 hrs.	Mean.
A 1	0.693	0.699	0.694	0.70	5.01	5.05	5.01	5.0
A 2	0.698	—	0.699	0.70	—	5.00	—	5.0
A 3	0.698	—	0.697	0.70	—	—	—	—
B	0.694	0.700	0.699	0.70	—	5.03	5.03	5.0
A + B	—	—	0.701	0.70	—	—	—	—

Benzene was freed from thiophen, washed, dried over calcium chloride, fractionated, and distilled from sodium before use. A uniform sample was used throughout.

"Pure" chloroform was washed with alkali, acid, and water, dried over calcium chloride, and twice distilled, and a constant boiling fraction was used.

The sealed solubility tubes were attached to a large paddle stirrer, which was rotated continuously in an electrically heated thermostat ( $25^{\circ} \pm 0.025^{\circ}$ ). Samples were taken, after settling, in 50 c.c. pipettes fitted with short removable glass tubes plugged with cotton wool.

The weighing bottles were dried to constant weight at 90°. Constant weighings ( $\pm 0.0002$  g.) were obtained by allowing the bottles, when removed from the oven, to stand in a desiccator over sulphuric acid for precisely 30 minutes, and by taking the final readings after the bottles had been on the balance for 2 minutes.

*Cryoscopic Measurements.*—In applying the test suggested by Sidgwick (J., 1915, 107, 672) for distinguishing between polymorphic, isomeric and tautomeric substances, solvents with low freezing points such as benzene and nitrobenzene could not be used, owing to the small solubilities of the acetyl derivatives in them and also to the long time required for saturation. Naphthalene was used and saturated solutions were obtained in a few minutes at a degree or two above its freezing point. Table II shows the results of these experiments.

TABLE II.

Substance.	Weight of solvent (g.).	Maximum depression.
A 1 alone .....	7.785	1.95°
After addition of B .....	"	1.90
B alone .....	7.780	1.95
After addition of A 1 .....	"	1.92

The determinations were carried out in a small Beckmann apparatus fitted with a thermometer graduated in tenths of a degree. This could be read to the nearest fortieth of a degree with ease.

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CLXXXVII.—*The Heat of Combustion of Salicylic Acid.*  
(A Reply to E. Berner.)

By PIETER EDUARD VERKADE and JAN COOPS.

DURING the last few years investigations on thermochemical standard substances, carried out in various places, have led to the adoption of benzoic acid, by international consent, as the exclusive standard substance to be used in determinations of heats of combustion. The value 6324 cal.<sub>15°</sub> per g. (air) ( $v = \text{constant}$ ), i.e., 6319 cal.<sub>15°</sub> per g. (vac.), has been accepted for the heat of combustion of this substance. At the same time, it was decided that, for scientific work, use should always be made of benzoic acid furnished for this purpose by the Bureau of Standards, Washington (*Compt. rend. de la troisième Conférence Internationale de la Chimie*, Lyons, 1922, p. 54; compare Verkade, *Chem. Weekblad*, 1922, 19, 389; 1924, 21, 13).

For some time we have tried to make it clear that this regulation is not quite sufficient. The heat capacity of a calorimetric system, found exclusively by means of this benzoic acid, is always somewhat uncertain; accidental errors, caused by contamination of the standard preparation, during packing or in the course of time, can be brought to light only with difficulty, if at all. We therefore emphasised strongly the desirability of introducing one or more further thermochemical standard substances (which, if so desired, could be considered as *secondary* standards) and, on the grounds of an extensive research, recommended salicylic acid for this purpose (Verkade and Coops, *Rec. trav. chim.*, 1924, 43, 561).

The heats of combustion of various samples of salicylic acid were determined with the following results, valid for an isothermal reaction at 19.5°, at constant volume and on the assumption that the above-mentioned heat of combustion of benzoic acid holds for the same temperature (compare Verkade, *Rec. trav. chim.*, 1925, 44, 799).

Sample.	Heat of combustion per g. (air).
Poulenc ("Standard pour calorimétrie") .....	5241.4 cal. <sub>15</sub> °
Merck ("Präparat von bestimmter Verbrennungswärme") .....	5241.7 "
Merck (crystallised from ether) .....	5241.3 "
Von Heyden ("Acid. Salicylicum recrystallis. puriss.") ..	5242.8 "
Kahlbaum ("für kalorimetrische Bestimmungen") .....	5242.6 "
Commercial ("Acid. Salicyl. praec. pulv.") (crystallised twice from water and once from chloroform) .....	5242.3 "

Thus a number of the purest samples obtainable commercially, most of them supplied especially for calorimetric purposes, furnished values for the heat of combustion which agreed within the error of observation. The heat of combustion of one of these samples remained unchanged when the substance was recrystallised from ether. A technical preparation taken from the Dutch market gave the same heat of combustion after purification. On the basis of these facts, we considered ourselves completely justified in regarding the mean of all our measurements as the heat of combustion of *pure salicylic acid*. This heat of combustion is 5241.9 cal.<sub>15</sub>° per g. (air) ( $v = \text{constant}$ ; 19.5°), *i.e.*, 5238.3 cal.<sub>15</sub>° per g. (vac.). The ratio of the heats of combustion of benzoic acid and salicylic acid is then  $6324/5241.9 = 1.2064$  (air).

Our work has recently been criticised by Berner (J., 1925, 127, 2747). Let it be said that this author shares our views regarding the desirability of introducing a second or secondary thermochemical standard substance and admits the particular suitability of salicylic acid for this purpose. However, we are said not to have taken the necessary care to ensure the greatest possible purity of our samples of salicylic acid and, on that account, to have found too high a heat of combustion; according to Berner, the heat of combustion of salicylic acid is only 5237.4 cal.<sub>15</sub>° per g. (air) ( $v = \text{constant}$ ; about 18°), *i.e.*, 5233.8 cal.<sub>15</sub>° per g. (vac.). The ratio of the heats of combustion of benzoic and salicylic acids should then be  $6324/5237.4 = 1.2075$  (air).

Berner seems to have overlooked the fact that the heat of combustion found by us was already confirmed from two sides :

1. Roth burnt salicylic acid in the micro-bomb and micro-calorimeter which he has constructed and found 5241.5 cal.<sub>15</sub>° per g. (air) for the heat of combustion, which deviates from our value by only — 0.08 part per 1000 parts (*Z. Elektrochem.*, 1924, 30, 607). Also, Roth has investigated salicylic acid in a bomb of normal dimensions and the well-known calorimetric apparatus of Stohmann-Hugershoff (*Naturwiss.*, 1924, 12, 652); it is, however, simply stated there that the heat of combustion found agreed exactly with ours. We have learned some details from a private

communication, which, by kind permission of Prof. Roth, we are able to publish. Various samples of salicylic acid from von Heyden gave concordant heats of combustion; an arbitrarily chosen commercial sample was purified by crystallisation from alcohol and after careful drying gave the same heat of combustion, which did not alter when the sample was recrystallised from alcohol and from water. The mean value of all these measurements was 5241.3 cal.<sub>15°</sub> per g. (air) ( $v = \text{constant}$ ; 18.3°); the deviation from our value amounted therefore to only  $-0.11$  part per 1000 parts.

2. Swientoslawski (*Bull. Soc. chim.*, 1925, 37, 84) found 5242.4 cal.<sub>15°</sub> per g. (air) for the heat of combustion of a commercial sample of salicylic acid, which was crystallised several times from water. This value deviates from ours only by about  $+0.10$  part per 1000 parts. Details of these measurements were not published.

These facts made it *a priori* scarcely possible for us to believe in the accuracy of Berner's results. It was improbable that the numerous preparations used by Verkade and Coops, by Roth, and by Swientoslawski—notwithstanding their different origins and different modes of purification—should all show a large surplus of exactly the same magnitude in the heat of combustion.

Nevertheless, we considered that our work ought to be controlled. In the first place, we again burnt one of the preparations which we had used previously (namely, that of Merck), making use of another bomb and of a calorimetric apparatus of considerably greater heat-capacity than that used previously. Secondly, we carefully subjected the previously used sample from von Heyden to various purification processes and measured the heat of combustion after each purification in the same apparatus. The results of these measurements are in the following table.

Material.	Heat of combustion per g. (air). ( $v = \text{constant}$ ; 19.5°).
Merck .....	5242.3
Von Heyden (crystallised twice from water, once from chloroform) .....	5241.4
Von Heyden (further crystallised from ether) .....	5241.5
„ (further crystallised from benzene) .....	5241.9

Thus we see that continued purification of von Heyden's salicylic acid brings about no change in the heat of combustion. The mean value of our 15 experiments with this acid in its various stages of purification is 5241.7 cal.<sub>15°</sub> per g. (air) ( $v = \text{constant}$ ; 19.5°). This new value for the heat of combustion of salicylic acid deviates from the one we found previously by only  $-0.04$  part per 1000 parts. For the ratio of the heats of combustion

of benzoic and salicylic acids we now obtain the value  $6324/5241 \cdot 7 = 1 \cdot 2065$  (air), which is practically identical with that found previously. We have no reason to doubt the correctness of this value, as the ratios of the heats of combustion of benzoic acid and naphthalene, and of benzoic acid and cane-sugar, obtained by us at about the same time (Verkade, Coops, and Hartman, *Rec. trav. chim.*, 1922, 41, 241; Verkade and Coops, *ibid.*, 1923, 42, 205) are in full agreement with those obtained recently in very careful work by other authors (Dickinson, *Bull. Bureau of Standards*, 1914, 11, 243; Swientoslawski and Starczewska, *Bull. Soc. chim.*, 1922, (4), 31, 654; Schläpfer and Fioroni, *Helv. Chim. Acta*, 1923, 6, 713), and at present generally accepted.

Hence we reach the conclusion that Berner found a value for the heat of combustion of salicylic acid which is too low, and that his results are subject to an error of about 0.8 part per 1000 parts. We are not able to indicate the cause of this error. At our request, Mr. Berner had the kindness to provide us with small quantities of two samples of salicylic acid which he had used in his research. These were the samples designated by Berner as 571II (Merck's acid, crystallised twice from water and once from chloroform) and 572IV (Kahlbaum D.A.B.5, subjected to sublimation in a vacuum and to several crystallisations from water, chloroform, and benzene). These samples yielded in our hands values for the heats of combustion of 5241.6 and 5241.9 cal.<sub>15</sub> per g. (air), respectively. These values are practically identical with those obtained by us for our own specimens. Berner as well as ourselves used benzoic acid from the Bureau of Standards, Washington (Standard Sample 396) in the calibration of the calorimetric apparatus.

As far as we know, Berner has not burnt standard samples of naphthalene and cane-sugar in his apparatus. The possibility therefore exists that, on burning these substances, this author may find, for the ratios mentioned above, values different from those now generally accepted as correct. In this case, the low heat of combustion of salicylic acid found by this author would be due to a slight error in the determination of the heat capacity of his apparatus.

#### EXPERIMENTAL.

The following alterations have been made in the calorimetric apparatus used for our previous measurements of the heat of combustion of salicylic acid (Verkade and Coops, *loc. cit.*) and described in detail in our first communication on heats of combustion of organic compounds (Verkade, Coops, and Hartman, *Rec. trav. chim.*, 1922, 41, 241).



We now used a silver calorimeter can of greater capacity than that used formerly, so that the quantity of water could be increased to about 2600 g., as well as a bomb of rustless V<sub>2</sub>A steel, supplied by the firm of Hugershoff, Leipzig, and especially suited, in our experience, for work of high precision.

For the method of carrying out the measurements reference may be made to the literature cited above.

*Heat Capacity of the Calorimetric Apparatus.*—This was determined by burning three samples of benzoic acid, namely, two standard preparations (Standard Samples 39a and 39b) from the Bureau of Standards, Washington, and one prepared by ourselves, which had already served for earlier work. At an oxygen pressure of 35 atms. the heat capacity was 3051.2 cal.<sub>15</sub> at a temperature of 19.5°. It seems unnecessary for us to give full details of our measurements, but we give a statement of results:

Sample.	Heat capacity.	Sample.	Heat capacity.
39a	3050.0	39b	3050.0
"	3049.6	"	3051.4
"	3051.4	"	3051.8
"	3051.6	"	3052.4
"	3051.3	Rotterdam	3050.9
"	3050.2	"	3052.3
"	3051.2	"	3051.8
		"	3052.5

For some observations regarding the heat capacity found in this way (*i.e.*, by the combustion of a standard substance), reference may be made to a paper by one of us (Verkade, *Rec. trav. chim.*, 1925, **44**, 799).

We were able to verify this heat capacity repeatedly by indirect methods, namely, by burning substances which we had already burnt before introducing the above-mentioned alterations in the calorimetric apparatus. Completely concordant results were obtained in both cases. Also (*e.g.*, in the case of *n*-butyl alcohol), we could obtain with our new apparatus complete concordance with the extremely accurate thermochemical work of Richards (compare Verkade and Coops, *Rec. trav. chim.*, 1926, in course of publication).

*Salicylic Acid Preparations.*—Von Heyden's "Acidum Salicylicum recrystallis. puriss" (used in our previous measurements) was crystallised twice from water. After drying in the air, it was very finely powdered and warmed to about 100° for 4 hours; during the heating it was again finely powdered several times. We have shown already (*Rec. trav. chim.*, 1924, **43**, 575) that salicylic acid can be heated for 20 hours at about 115° without undergoing even the slightest decomposition. This heating is necessary, since it has

been shown recently (*e.g.*, Cohen, Verkade, Saburo Miyake, Coops, and van der Hoeve, *Versl. Kon. Akad. Wetensch. Amsterdam*, 1926, **35**, 48) that on crystallisation from water, salicylic acid may occlude several parts of water per thousand, which is not removed even by very long drying in a vacuum over phosphorus pentoxide. However, this occluded water can be removed for the most part in the way described above, as was proved by determinations of the heat of combustion carried out expressly for this purpose. The sample obtained in this way was then recrystallised from dry chloroform (sample II); the last traces of water in the crystals were removed by distilling off a part of the solvent from the boiling solution, the water then passing over with the solvent. After a part of this sample had been burnt, the remainder was crystallised from dry ether (sample III) and finally from dry benzene (sample IV). All three samples were finely powdered and dried for several days in a vacuum over phosphorus pentoxide.

Merck's salicylic acid ("Präparat von bestimmter Verbrennungswärme") and Berner's samples 571II and 572IV were finely powdered and dried in the same way without other treatment.

*Heat of Combustion of the Salicylic Acid Preparations.*—On account of a small difference in the composition of the products of combustion of benzoic and salicylic acids, a correction of +0.1 cal.<sub>15</sub> must be introduced in the above-mentioned heat capacity in combustions of the latter acid (compare *Rec. trav. chim.*, 1924, **43**, 566). We shall give no details of the measurements. We found the following values for the heat of combustion of salicylic acid per g. (air) ( $v = \text{constant}$ ; 19.5°).

Sample.	Heat of combustion.	Mean.
Merck	5242.4, 5242.7, 5240.7, 5242.4, 5243.2	5242.3
II	5241.5, 5241.8, 5242.2, 5240.0, 5241.6	5241.4
III	5242.5, 5242.5, 5240.4, 5241.5, 5240.8	5241.5
IV	5242.6, 5240.8, 5241.6, 5241.7, 5242.9	5241.9
571 II	5241.6, 5241.5, 5241.7	5241.6
572 IV	5241.2, 5240.1, 5244.5	5241.9

### *Summary.*

Our previous determinations of the heat of combustion of salicylic acid have been submitted to a control. The heat of combustion of this compound was found to be 5241.7 cal.<sub>15</sub> per g. (air) ( $v = \text{constant}$ ; 19.5°), a value practically identical with that found previously. Hence the heat of combustion found by Berner, namely, 5237.4 cal.<sub>15</sub> per g. (air) ( $v = \text{constant}$ ; about 18°), is too low.

This investigation was carried out with the aid of a grant from

the "Hoogewerff Fonds" and we take this opportunity of expressing our thanks to the Advisory Board of this Fund for the support we have received.

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## CLXXXVIII.—As-Chlorotetrahydroarsinoline and Some Quaternary Arsonium Compounds.

By ELWYN ROBERTS, EUSTACE EBENEZER TURNER, and (in part)  
FRANK WARD BURY.

As-METHYLTETRAHYDROARSINOLINE (Burrows and Turner, J., 1921, 119, 426) readily forms a *dichloride*, which, when heated, is smoothly decomposed to give As-chlorotetrahydroarsinoline, the first simple cyclic chloroarsine of this series to be prepared.

Attempts to prepare arsinolines and arsinolines (or the corresponding intermediate compounds) are described in this paper.

The alternation in the physical properties of a series of benzene derivatives having normal side-chains is a subject of considerable interest. The following table shows that there is a marked alternation in the melting points of the first five members of the series of methiodides of the general formula  $\text{Ph} \cdot [\text{CH}_2]_x \cdot \text{AsMe}_3\text{I}$ .

$\text{Ph} \cdot \text{AsMe}_3\text{I}$ .....	252°	$\text{Ph} \cdot [\text{CH}_2]_3 \cdot \text{AsMe}_3\text{I}$ .....	144°
$\text{Ph} \cdot \text{CH}_2 \cdot \text{AsMe}_3\text{I}$ .....	194—195	$\text{Ph} \cdot [\text{CH}_2]_4 \cdot \text{AsMe}_3\text{I}$ .....	150—151
$\text{Ph} \cdot [\text{CH}_2]_2 \cdot \text{AsMe}_3\text{I}$ .....	203—204*		

\* Previously given (Turner and Bury, J., 1923, 123, 2489) as 200°.

There is also a marked difference in the ease with which the five arsinolines of the type  $\text{Ph} \cdot [\text{CH}_2]_x \cdot \text{AsMe}_2$  are prepared by the interaction of the appropriate Grignard reagent and dimethyl-iodoarsine. The respective percentage yields of phenyl-, phenyl-propyl-, phenylbutyl-, phenylethyl-, and benzyl-dimethylarsine were 80, 65, 45, 45 (97\*), and 20. We regard a low yield as being due to a high tendency, on the part of the arsine, to undergo oxidation, and conversely; we have, however, not conducted quantitative measurements on the subject.

[With F. W. BURY.] In view of the success achieved by Rosenheim and Plato (*Ber.*, 1925, 58, 2000) and by Mills and Raper (J., 1925, 127, 2479), experiments on the resolution of arsenic compounds in progress in this laboratory have been discontinued. Two asymmetric types were under examination; it has been found

\* Preparation carried out in an inert atmosphere (Turner and Bury, *loc. cit.*).

impossible to resolve cyclohexylphenylbenzylmethyldarsonium d- $\alpha$ -bromocamphor- $\pi$ -sulphonate and the phenylbenzylarsinates of strychnine and l-menthylamine. One or two compounds prepared incidentally are, however, now described.

#### EXPERIMENTAL.

*$\gamma$ -Phenylpropyldimethylarsine.*—The dimethyliodoarsine required for this preparation (Burrows and Turner, *loc. cit.*) is most conveniently obtained by passing sulphur dioxide into a solution containing 225 g. of cacodylic acid, 450 g. of potassium iodide, 150 g. of concentrated sulphuric acid, and 1850 c.c. of water.  *$\gamma$ -Phenylpropyldimethylethylarsonium iodide* is formed fairly readily from the arsine and methyl iodide, and separates from alcohol-ether in colourless leaflets, m. p. 118° (Found: I, 33.3.  $C_{13}H_{22}IA$ s requires I, 33.4%).

*$\gamma$ -Phenylpropylmethylchloroarsine* was heated at 200° in a current of dry carbon dioxide, but although it underwent considerable apparent change, no hydrogen chloride was evolved. This is in interesting contrast to the ease with which o-phenoxyphenyldichloroarsine passes into 10-chlorophenoxarsine (Roberts and Turner, J., 1925, 127, 2004).

*Derivatives of As-Methyltetrahydroarsindole.*—The methiodide melts at 239–240°, not at 235°, as previously recorded. The ethiodide is less readily formed than the methiodide, and separates from ether-alcohol in colourless prisms, m. p. 185–186° (Found: I, 34.8.  $C_{12}H_{13}IA$ s requires I, 34.9%). The benzobromide is formed as a glassy mass when the components are warmed together, and is difficult to purify. It crystallises from ether-alcohol in colourless prisms, m. p. 210–211° (Found: Br, 19.9.  $C_{17}H_{20}BrAs$  requires Br, 21.1%).

When the arsinoline was treated with 1 mol. of bromine, and the product with alkali, no *As*-oxide could be detected. The main product was  $\gamma$ -phenylpropyl bromide.

*As-Chlorotetrahydroarsinoline.*—*As*-Methyltetrahydroarsinoline (20 g.) was dissolved in carbon tetrachloride, and a current of dry chlorine allowed to impinge on the surface of the solution. The white solid *dichloride* separated rapidly, and when a slight excess of chlorine was present the mixture was rendered colourless by addition of a drop of arsinoline. The carbon tetrachloride was removed by distillation, and the residue distilled under diminished pressure. Evolution of methyl chloride was regular and rapid, and as soon as it was complete a preliminary fraction distilled at 120–150°/21 mm., and then the whole of the residue at 155°/16 mm. (16 g.). The latter crystallised on cooling, to give large, irregular, hexagonal

rhombs, m. p.  $22^{\circ}$ , and was pure As-chlorotetrahydroarsinoline (Found: Cl, 15.4.  $C_9H_{10}ClAs$  requires Cl, 15.5%).

When a solution of the chloroarsine in diethylaniline was boiled for 5 hours, marked decomposition occurred, but no 3:4-dihydroarsinoline was isolated from the product. A small quantity of an arsine was formed, since the distilled product combined or reacted with methyl iodide.

*Benzyl dimethylarsine*.—Magnesium benzyl chloride reacted smoothly with one equivalent of dimethyliodoarsine. The product was worked up in the usual manner. The final ethereal solution remained clear while being dried over sodium sulphate, but, when filtered, became cloudy. This was due to oxidation and not to the presence of an additive compound with dimethyliodoarsine, since the ethereal solution had, in accordance with usual practice, been washed with alkali. The arsine was finally obtained as a colourless liquid, b. p.  $110^{\circ}/8$  mm. The yield (20%) would probably be improved by carrying out all the operations in an inert atmosphere (compare Turner and Bury, *loc. cit.*).

The *methiodide* is formed readily, and separates from alcohol in colourless leaflets, m. p.  $195$ — $196^{\circ}$  (Found: I, 37.4.  $C_{10}H_{16}IAs$  requires I, 37.6%). The *ethiodide*, formed moderately readily, crystallises from alcohol-ether in colourless leaflets, m. p.  $163$ — $165^{\circ}$  (Found: I, 36.3.  $C_{11}H_{18}IAs$  requires I, 36.1%).

*$\delta$ -Phenyl- $n$ -butyl dimethylarsine*.—This was prepared from  $\gamma$ -phenylpropyl bromide, *via* the corresponding nitrile (von Braun, *Ber.*, 1910, 43, 2843; Rupe, *Annalen*, 1912, 395, 87),  $\delta$ -phenyl- $n$ -butyl alcohol, and  $\delta$ -phenyl- $n$ -butyl bromide (von Braun, *Ber.*, 1911, 44, 2871).

The bromide readily formed a Grignard reagent; this reacted smoothly with dimethyliodoarsine to give a product which, after the usual treatment, including washing with alkali, afforded the arsine as a colourless liquid, b. p.  $150^{\circ}/14$  mm. (yield, 45%).

The *methiodide* is very readily formed, and is sparingly soluble in alcohol, from which it crystallises in colourless leaflets, m. p.  $150$ — $151^{\circ}$  (Found: I, 33.0.  $C_{13}H_{22}IAs$  requires I, 33.4%).

The *ethiodide*, formed moderately easily, separates from alcohol in leaflets, m. p.  $134$ — $135^{\circ}$  (Found: I, 32.5.  $C_{13}H_{24}IAs$  requires I, 32.2%).

*Phenyl- $\beta$ -phenylethyl methylarsine*.—This substance was readily obtained by the interaction of magnesium  $\beta$ -phenylethyl bromide and phenylmethyliodoarsine in ethereal solution. When the ethereal extract of the arsine, obtained by the usual method, was evaporated, a considerable quantity of a gummy solid separated. This was removed before distilling the arsine under diminished

pressure. *Phenyl-β-phenylethylmethylarsine* is a colourless liquid boiling at 187°/12 mm. and 190°/15 mm., and was obtained in 82% yield.

The *methiodide* is formed readily, and crystallises from water in rhombohedra or prisms, m. p. 119° (Found: I, 30.5.  $C_{16}H_{20}IAs$  requires I, 30.6%).

*Action of β-Phenylethyl Bromide on Arsenites and Arsinites.*—

(a) *On sodium arsenite.* A solution of arsenious oxide (0.5 mol.) in aqueous sodium hydroxide (3 mols.) was boiled with the bromide for several days, under reflux. Some bromide was recovered unchanged, and no arsenic acid could be detected in the product.

(b) *On sodium arsenite in presence of copper bronze.* The bromide was stirred and heated at 140—180° for 7 hours in presence of dry sodium arsenite (Kahlbaum) and copper bronze. No change was observed. (c) *On potassium methylarsinite.* An aqueous-alcoholic solution containing methylarsenious oxide (1 mol.), potassium hydroxide (2 mols.), and the bromide (1 mol.) was boiled under reflux for 2 days. Styrene, but no arsenic acid, was formed.

[With F. W. BURY.] *Dicyclohexylphenylarsine.*—This was prepared by adding phenyldichloroarsine to a solution of magnesium cyclohexyl bromide, the reaction product being worked up in the usual manner. The arsine is a colourless liquid, b. p. 220°/14 mm. The *methiodide* and *ethiodide* are formed readily and crystallise from alcohol-ether in prisms, m. p. 187° (Found: I, 27.5.  $C_{19}H_{30}IAs$  requires I, 27.6%), and plates, m. p. 188—189° (Found: I, 26.6.  $C_{20}H_{32}IAs$  requires I, 26.8%), respectively.

*Tricyclohexylarsine.*—When arsenious iodide was added to an ethereal solution of magnesium cyclohexyl chloride or bromide, only half of the calculated quantity reacted. The arsine was, however, obtained mixed with a little dicyclohexyl as a colourless oil, b. p. 235°/12 mm. The *methiodide* was formed readily and crystallised from water in prisms, m. p. 153—154°. The *benzobromide* melts at 197° with slight decomposition (Found: Br, 16.2.  $C_{25}H_{40}BrAs$  requires Br, 16.2%).

*cycloHexylphenylmethylarsine.*—A Grignard reagent prepared from 24 g. of cyclohexyl chloride was treated with phenylmethyl-iodoarsine until the yellow colour of the latter persisted, *i. e.*, when about 75% of the iodo-compound had been added. The reaction product was worked up as usual, and gave 30 g. of *cyclohexylphenylmethylarsine* as a highly refractive oil, b. p. 152—153°/12 mm., having no marked tendency to oxidise.

When the arsine was heated at 100° with one equivalent of benzyl bromide and a little alcohol, large, colourless crystals began to form, but subsequently disappeared. On cooling, only a little white

powder separated, and crystallisation was induced by addition of excess of ether. *cycloHexylphenylbenzylmethyларsonium bromide* was thus obtained; recrystallised from alcohol-ether, it formed rectangular plates, m. p. 193° (Found: Br, 19.0.  $C_{20}H_{26}BrAs$  requires Br, 19.0%).

The corresponding *d-α-bromocamphor-π-sulphonate* was prepared. The crude material melted at 109–113°, and crystallisation experiments gave unpromising results, mixtures of crystalline, amorphous, and gel-like material being obtained.

*Phenylbenzylarsinic Acid*.—Excellent yields of this acid are obtained by the following method, which is more expeditious than that described by Bertheim (*Ber.*, 1915, 48, 350): Crude phenylarsenious oxide (75 g.) as obtained from phenyldichloroarsine and sodium hydroxide was dissolved in 150 c.c. of methylated spirit. Sodium hydroxide (36 g.) in 52 c.c. of water was added. To the hot solution, 60 g. of benzyl chloride were added gradually, keeping the initial vigorous reaction in progress. Sodium chloride separated at once. The mixture was left until cold, freed from alcohol by distillation, acidified, and the resulting precipitate of acid washed with water and ether.

*Strychnine Phenylbenzylarsinate*.—This salt was prepared by mixing hot alcoholic solutions of the base and the acid, and formed colourless needles (Found: N, 4.5; As, 11.4, 11.4.

$C_{21}H_{22}O_2N_2 \cdot C_{13}H_{13}O_2As \cdot 3H_2O$   
requires N, 4.2; As, 11.3%). It had  $[\alpha]_D^{20} - 31.2^\circ$  in 50% aqueous acetone, and when crystallised from this solvent gave a mixture of free acid and strychnine salt. When hot alcoholic solutions of strychnine (1 mol.) and the acid (2 mols.) were mixed, the free acid separated first.

*1-Menthylamine Phenylbenzylarsinate*.—Equivalent quantities of the base and acid were together dissolved in alcohol, and the solution was allowed to evaporate in a vacuum over sulphuric acid. The whole set to a mass of hairy needles. These were collected, dissolved in benzene, and the solution treated with light petroleum; a crystalline precipitate was obtained, which consisted of a mixture of base and acid.

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CLXXXIX.—*The Resin of Hevea Rubber.*

By GEORGE STAFFORD WHITBY, JACOB DOLID, and FREDERIC HARRISON YORSTON.

THE circumstance that the resin of the rubber from *Hevea brasiliensis* constitutes only a small proportion of the weight of the rubber (on the average, about 2.80%. Compare van Rossem, *Koll.-Chem. Beih.*, 1918, 10, 52; "The Quality of Plantation Rubber," Imp. Inst., 1922, pp. 13, 27, 88, 95) and is of a sticky, semi-fluid consistency has apparently deterred investigators from subjecting it to chemical examination (compare, e.g., Tschirch and Müller, *Arch. Pharm.*, 1905, 243, 141), and when the present investigation was begun but little was known concerning its chemical nature.

It has now been shown that, contrary to Hinrichsen and Kindscher's statement (*Z. angew. Chem.*, 1910, 23, 49), the resin contains several optically active substances (all lævorotatory, with the exception of an amino-acid occurring in very small amounts only) and that sterol substances are present. Hillen's failure to obtain sterol colour reactions (*Arch. Pharm.*, 1913, 251, 94) was probably due to interference of other substances present in the crude extract. Cohen (*Arch. Pharm.*, 1908, 246, 520) examined the resin for lupeol, with negative results. Hinrichsen and Kindscher (*loc. cit.*) found the resin to be largely saponifiable, and Dekker (*Koll.-Chem. Beih.*, 1918, 10, 54), who confirmed this finding, obtained the data shown in the first two columns below. The figures in the third column, which have been added, would seem to suggest that the differences in the percentage of extract unsaponifiable in different forms of *Hevea* rubber are due to differences in the amount of saponifiable matter rather than to differences in the amount of unsaponifiable matter.

Form of rubber.	Acetone extract %.	% extract unsaponifiable.	% unsaponifiable in the rubber.
Fine hard Para .....	3.0	25.4	0.76
Sheet .....	1.8	48.3	0.87
Crêpe .....	3.2	22.0	0.705

A sample of the resin was found by Hinrichsen and Kindscher (*loc. cit.*) to show an iodine absorption of 118%. Beadle and Stevens (*Internat. Cong. Appd. Chem.*, 1912, 24, 581) reported that the resin was partly water-soluble. The presence in it of nitrogenous material was mentioned by Spence and Kratz (*Kolloid-Z.*, 1914, 14, p. 268, footnote), and was confirmed by Dekker (*Meded. Delft*, 1916, 506) by an indirect method. Dekker found acetone extraction to reduce the nitrogen content of two samples of *Hevea* crêpe by 0.051 and 0.029%, respectively, and of a sample of *Hevea* sheet by 0.014%.



Working with a sufficiently large amount of the acetone extract of *Hevea* rubber, the present authors have isolated and identified a sterol, a sterol ester, a sterol glucoside, *d*-valine, quebrachitol, and stearic acid and the liquids, oleic and linoleic acids. The amounts and ratios in which the substances occur vary in different rubber samples. The mixture of unsaturated, liquid fatty acids occurs in much larger amount than any of the other constituents. Titration of the acetone extract of twenty-four samples of smoked sheet and pale crêpe rubber showed that the average total acid content was equivalent to 0.272 g. of potassium hydroxide per 100 g. of rubber. Hence, if the mean molecular weight of the acids is taken as 280, the total acid content of average samples of latex *Hevea* rubber is of the order of 1.4% of the weight of the rubber or roughly one-half of the weight of the acetone extract.

The total amount of solid material which it was actually possible to crystallise from the extract was about 0.65% of the weight of the rubber. As the resin content of the crêpe from which most of the resin examined was obtained was 2.71%, it may be said that of this about 1.9 (=1.25 + 0.65) was definitely accounted for. The balance of about 0.8% represented losses together with unidentified constituents of the liquid, uncrystallisable portion of the resin.

The order of magnitude (%) in which the recognised constituents of *Hevea* resin occurred was estimated roughly as follows :

Sterol ester .....	0.075	Quebrachitol .....	very small amount
Sterol glucoside .....	0.175	Stearic acid .....	0.15
Sterol .....	0.225	Oleic acid .....	} 1.25
<i>d</i> -Valine .....	0.015	Linoleic acid .....	

The high proportion of free fatty acid in the resin of *Hevea* rubber makes this resin unique, not only among the resins of rubbers of various botanical origins, but also among resins in general. In *Hevea* resin, fatty acids predominate, and hence it has a softer consistency, a higher saponification value, and a smaller optical activity than have other rubber resins, in which optically active, unsaponifiable, crystalline substances predominate. The resins obtained by extracting plants with organic solvents contain free fatty acids in a good many cases, but never in large proportions (Power and his co-workers, J., various papers).

The question of the mode of association of the resin constituents with the hydrocarbon in rubber is of some interest. It is probable that the fatty acids occur in solution in the caoutchouc. Rubber, both raw and vulcanised, swells considerably when placed in oleic acid, linoleic acid, molten stearic acid, or the mixed liquid fatty acids actually isolated from *Hevea* rubber. Thus, for example, a sample of smoked sheet placed in the last-mentioned medium

imbibed 4.04 times its weight after 7 days. The sterol glucoside found in rubber is insoluble in all the usual laboratory solvents, including benzene. It probably occurs, not dissolved in the caoutchouc, but in solution in the fatty acids, for the authors have observed that it will dissolve on warming in fatty acids, except in the lowest members, yielding sols which often gel on cooling.

The resin, and especially the fatty acids which it comprises, influence the behaviour of rubber in several important ways (compare Whitby, *Trans. Inst. Rubber Ind.*, 1925, 1, 12; Whitby and Jane, *Second Colloid Symposium Monograph*, 1925, 16).

#### EXPERIMENTAL.

Samples of rubber were extracted with acetone in a large, heavily galvanised iron extractor of the Soxhlet type, 3 ft. high and 1 ft. in diameter. The thimble, which is large enough to hold about 4.5 kg. of rubber, is suspended directly in the vapour of the boiling extractant. The condenser, which sits on a flange at the top of the main extraction vessel, consists of a hollow cone and head through which water circulates and a separate, conical coil of block tin round the cone. The metal of the extractor was attacked slightly in the course of time, zinc salts of fatty acids being found in the extract.

The extracts from a number of different samples of rubber (crêpe, smoked sheet, slab crêpe) were examined. The procedure varied somewhat in different cases, as the proportions of the constituents were not identical in different batches, but in general it was as follows: The batch of rubber was extracted for 70 to 100 hours. The solution was concentrated to about 600 c.c. per kg. of rubber and kept for a week or so at or below 0°. The solid which separated (Fraction A) was removed and the solution (and washings) was concentrated to one-third or less of its volume and again kept in the cold for a week. The solid which separated (Fraction B) was removed and washed with a little cold acetone. The solution and washings were then evaporated on the water-bath to remove as much acetone as possible. The viscous liquid residue is called the Liquid Fraction.

##### *Fraction A.*

This fraction (47 g. of a light brown powder from 21.7 kg. of pale latex crêpe) was separated into a chloroform-soluble sterol ester, a water-soluble amino-acid and quebrachitol, and an insoluble sterolin.

*Sterol Ester.*—Chloroform extracted from fraction A about 10 g. of a sterol ester which, after recrystallisation from alcohol, had  $m.p. 83^{\circ}$  and  $[\alpha]_D^{25} - 11.1^{\circ}$ ,  $-10.8^{\circ}$  (0.2145 and 0.2303 g. in 15 c.c.

of chloroform) (Found: C, 83.0; H, 12.6; iodine absorption, 34.3.  $C_{17}H_{33}O_2 \cdot C_{27}H_{45}$  requires C, 82.8; H, 12.4; iodine absorption, 39.6%). The iodine absorption is due to unsaturation of the sterol part of the ester, the acid part being saturated. (The iodine values obtained for sterols are usually somewhat lower than the calculated values.) The *sterol* obtained by hydrolysing the ester with alcoholic potassium hydroxide crystallised from alcohol in fine, white needles, m. p. 133—134°,  $[\alpha]_D^{25} - 23.2^\circ$  (0.3140 g. in 15 c.c. of chloroform) (Found: C, 82.8; H, 11.4.  $C_{27}H_{46}O$  requires C, 83.9; H, 11.9%) and gave the usual colour reactions and also certain new reactions (Whitby, *Biochem. J.*, 1923, **17**, 5). The acetate crystallised from alcohol in matted crystals, m. p. 113—114°, and gave  $[\alpha]_D^{25} - 18.8^\circ$  (0.1707 g. in 15 c.c. of chloroform). The *acid* obtained by hydrolysis of the sterol ester melted at 73—75° after recrystallisation from alcohol and appeared to have the composition  $C_{17}H_{34}O_2$  (Found: C, 74.5; H, 11.2. Calc.: C, 75.6; H, 12.6%. Found for the *silver* salt: Ag, 28.5.  $C_{17}H_{33}O_2Ag$  requires Ag, 28.5%).

The sterol ester isolated from slab rubber and from smoked sheet melted at 102° and 91—93°, respectively, but the amounts isolated were insufficient for careful examination.

*The Aqueous Extract.*—Addition of alcohol to the concentrated aqueous extract of fraction A (derived from 21.7 kg. of crêpe) precipitated 1 g. of an amino-acid; quebrachitol remained in solution. The two substances could also be separated by precipitating the amino-acid with mercuric nitrate or by evaporating the aqueous extract to dryness and extracting the amino-acid with cold alcoholic hydrochloric acid.

The amino-acid, m. p. about 260° (decomp.), gave (a) the ninhydrin reaction, (b) the pine splinter pyrrole reaction, when heated either alone or with zinc dust, and (c) a blue colour with phenol and sodium hypochlorite (Found: C, 52.2; H, 9.42; amino-N, by micro-van Slyke method, 11.7, 11.6.  $C_5H_{11}O_2N$  requires C, 51.3; H, 9.4; N, 11.9%). It had  $[\alpha]_D^{25} + 22.9^\circ$ ;  $[\alpha]_D^{25} + 26.5^\circ$  (0.1888 g. in 25 c.c. of 20% HCl). For a 3% solution of *d*-valine in 20% HCl, E. Fischer (*Ber.*, 1906, **39**, 2325) obtained  $[\alpha]_D^{25} + 28.8^\circ$ . The total amino-nitrogen in an aqueous extract of the original rubber was 0.0015% (micro-van Slyke method). This corresponds to 0.0126% of valine in the rubber or 0.46% of valine in the acetone extract.

Quebrachitol was first noticed as separating in well-formed crystals from the acetone extract of a sample of smoked sheet which had stood for a long time after the separation of a first fraction. It had m. p. 190° and  $[\alpha]_D^{20} - 80.3^\circ$  (0.2800 g. in 14.5 c.c. of water).

It was subsequently always recognised in fraction A, and in several cases was actually isolated from it.

By means of Scherer's test for inositol (*Annalen*, 1852, **81**, 375; compare Boedker, *Zig. nat. Med.*, **10**, 162) the presence of quebrachitol was detected in forty-five samples of *Hevea* rubber comprising all the usual forms (latex crêpe, lower grade crêpes, smoked sheet, fine hard Para, etc.). For most of these samples the authors are indebted to Dr. O. de Vries. A few grams of the rubber (as little as 1 g. will give a positive result), cut into small pieces, were boiled for 15–30 minutes with glacial acetic acid, which was then evaporated, finally on a water-bath. The material extracted from the residue by a little hot water developed a rose-red colour after the usual nitric acid-calcium chloride treatment.

The isolation of quebrachitol from the latex of *H. brasiliensis* has been recorded by De Jong (*Rec. trav. chim.*, 1906, **25**, 48), and from rubber by Pickles and Whitfield (*P.*, 1911, **27**, 54).

Professor R. P. D. Graham has kindly made crystallographic measurements on some of the crystals which separated from the acetone extract and on larger crystals of quebrachitol which had grown in a sample of evaporated latex serum which had been kept for 9 years. For comparison, there are given below the crystallographic data obtained by Anderson with a sample of quebrachitol isolated by Petrie from *Heterodendron oleaefolium*, Desf. (*Proc. Linnean Soc. N.S. Wales*, 1918, **43**, 857).

*Crystallographic data for l-inositol methyl ether* (by R. P. D. GRAHAM). The crystals were transparent, colourless blades, sometimes attaining a length of 6 mm. or more. *System*: orthorhombic. No cleavage was observed. *Forms and habit*: All the crystals measured exhibited the forms  $a(100)$ ,  $b(010)$ ,  $m(110)$ , and  $q(011)$ . On several of the crystals there were in addition very small facets of the form  $(101)$ . The crystals were elongated in the direction of the vertical axis, and tabular parallel to  $a$  or  $m$ . The faces of the orthorhombic prism,  $m$ , were heavily striated vertically, with a tendency to curvature; but faces of the other forms were smooth and yielded fair reflexions. A peculiarity of the crystals was that, in nearly all the cases observed, only two opposite faces of the prism  $m$  were developed.

*Angular measurements and axial ratios.*

	Limits.	No.	Mean.	Calc.	Anderson.
$b\ m$	52° 26'—53° 19'	5	52° 47'		52° 44'
$c\ q$	39 10—39 35	6	39 22		39 26
$c$	47° 03'	1	47 03	47° 13'	47 43

*Axial ratios*  $a : b : c = 0.7595 : 1 : 0.8204$

0.7609 : 1 : 0.8224 (Anderson).

*The Sterolin.*—The residue of fraction A after removal of the chloroform- and water-soluble portions consisted in all cases of sterol glucoside. After purification through its acetate, it had m. p. 285–290° (decomp.) and  $[\alpha]_D^{25} - 41.7^\circ$  (0.2900 g. in 14.6 c.c. of pyridine) (Found: C, 73.0; H, 10.4.  $C_{33}H_{56}O_6$  requires C, 72.3; H, 10.2%). Its behaviour in the sterol colour reactions and in a new test which enables sterolins to be distinguished from sterols has been described elsewhere (Whitby, *Biochem. J.*, 1923, 17, 5). The *acetate*, prepared by means of hot acetic anhydride, crystallised from alcohol in pearly leaflets, m. p. 165°;  $[\alpha]_D^{25} - 22.4$  (Found: C, 69.1; H, 9.0; Ac, 23.1.  $C_{33}H_{52}O_6Ac_4$  requires C, 68.7; H, 8.9; Ac, 22.5%). The *benzoate* was prepared by treating a pyridine solution of the sterolin with a slight excess of benzoyl chloride, extracting the diluted reaction mixture with ether, and washing the extract with dilute sulphuric acid, dilute potassium hydroxide, and water in succession. The product, recrystallised from ether, had m. p. 198° and  $[\alpha]_D^{25} + 15.7^\circ$ ,  $+ 16.1^\circ$  (0.3256, 0.2637 g., respectively, in 15 c.c. of chloroform).

Hydrolysis of the sterolin by hydrochloric acid in amyl alcohol by Power and Salway's method (J., 1913, 103, 399) gave glucose (osazone, m. p. 201°) and a sterol. The latter, obtained as lustrous plates after recrystallisation, melted at 134.5° and had  $[\alpha]_D^{25} - 31.7^\circ$ ,  $- 32.1^\circ$  (0.2793 and 0.1268 g., respectively, in 15 c.c. of chloroform) (Found: C, 84.3; H, 12.3.  $C_{27}H_{46}O$  requires C, 83.9; H, 11.9%). The acetate of this sterol melted at 115° and showed  $[\alpha]_D^{25} - 38.6^\circ$  (0.0634 g. in 15 c.c. of chloroform). There is little doubt that the sterolin is sitosterol *d*-glucoside (Power and Salway, *loc. cit.*, p. 1022).

The sterol glucosides are soluble, not only in hot amyl alcohol and in pyridine (Power and Salway, *loc. cit.*, p. 399), but also in amines (piperidine and diethylamine), fatty acids (octoic acid), mustard oils (phenylthiocarbimide), and higher ethers (anisole). In many of such liquids the sols set to gels on cooling.

#### Fraction B.

This fraction usually consisted of a mixture of a sterol or sterols and one or more saturated fatty acids. Separation was effected by treating the mixture with alcoholic potassium hydroxide and then extracting the sterol by ether from the mixture of potassium salt and sterol which came out on cooling. In certain cases, either the sterol or the fatty acid predominated so greatly that recrystallisation was sufficient to obtain it in a pure condition.

*The Sterol.*—A sterol was first isolated from the acetone extract of a batch of 4 kg. of smoked sheet rubber, which, when concentrated to 500 c.c. per kg. and kept in the cold, deposited 9 g. of

almost pure sterol as rosettes of crystals. After recrystallisation six times from alcohol, there was obtained a mass of matted, white leaflets, m. p.  $125^{\circ}$ ,  $[\alpha]_D^{25} = -24.6^{\circ}$  (0.2975 g. in 15 c.c. of chloroform) (Found: C, 83.8; H, 13.0.  $C_{27}H_{46}O$  requires C, 83.9; H, 11.9%).

Fischer's method (*Ber.*, 1913, **46**, 4029) of preparing penta-acyl derivatives of sugars is suitable for the acylation of sterols, including cholesterol. The *benzoate*: The sterol described above was treated in chloroform solution with a slight excess of benzoyl chloride and an equivalent amount of quinoline. After a short time, the solution was washed successively with dilute sulphuric acid, dilute sodium hydroxide solution, and water, dried over calcium chloride, and the chloroform evaporated. The residue crystallised from alcohol-chloroform in lustrous plates, m. p.  $144-145^{\circ}$ ;  $[\alpha]_D^{25} = -20.7^{\circ}$  (0.1340 g. in 14.6 c.c. of chloroform) (Found: C, 83.9; H, 9.9.  $C_{27}H_{45}O \cdot CO \cdot C_6H_5$  requires C, 83.3; H, 10.2%). The *propionate*, prepared by a similar method, crystallised from alcohol in lustrous white plates, m. p.  $98^{\circ}$ ;  $[\alpha]_D^{25} = -29.4^{\circ}$  (0.2005 g. in 17 c.c. of chloroform). The *acetate*, prepared by treating the sterol with an excess of acetic anhydride, was obtained as white plates or leaflets, m. p.  $114-115^{\circ}$ ;  $[\alpha]_D^{25} = -30.6^{\circ}$  (0.3169 g. in 14.6 c.c. of chloroform).

A sample of sterol obtained, in the case of a batch of 21.7 kg. of pale latex crêpe, by extracting a mixture of potassium soap and sterol with ether was freed from potassium salt by converting this into the silver salt and extracting the sterol with ether. After several recrystallisations from ether, the sterol was obtained as lustrous plates, m. p.  $134-135^{\circ}$ ;  $[\alpha]_D^{25} = -21.4^{\circ}$  (0.3278 g. in 15 c.c. of chloroform). The *benzoate* had m. p.  $144.5^{\circ}$ , and  $[\alpha]_D^{25} = -12.5^{\circ}$  (0.2393 g. in 15 c.c. of chloroform) (Found: C, 83.1; H, 10.2.  $C_{34}H_{50}O_2$  requires C, 83.3; H, 10.2%).

From the acetone extract of a sample of slab rubber, not quite the whole of the sterol separated when the extract was kept at a suitable concentration. The extract was then saponified, and from the unsaponifiable material ether removed a sterol, m. p.  $133-134^{\circ}$ .

*The Fatty Acid.*—The main fatty acid present in fraction B, previously regarded as a  $C_{20}$  saturated fatty acid and named "heveic acid" (Whitby, *Brit. Assoc. Rep.*, 1923, 432), has now been identified as stearic acid. A sample (equiv., 291) isolated from slab rubber melted at  $65.5-66.5^{\circ}$  after recrystallisation from alcohol and at  $68.5^{\circ}$  after recrystallisation from aqueous acetic acid, benzene, aqueous acetone, and light petroleum in succession. It was then mixed with further quantities of solid acid obtained from crêpe rubber, recrystallised until its melting point was  $67.5-68.5^{\circ}$ , and converted, by treatment of the silver salt with ethyl

iodide in benzene, into the ethyl ester. This after purification had m. p. 32.5—33.5° and  $n_D^{40}$  1.4292. The acid regenerated therefrom had m. p. 68—69° (alone or mixed with stearic acid),  $n_D^{20}$  1.4332,  $n_D^{80}$  1.4300 ( $n_D^{20}$  for stearic acid in the same apparatus, 1.4328). A sample of the ester prepared from the solid acid derived from another sample of rubber had, after distillation and recrystallisation from chloroform, m. p. 31.5° (Found:  $M$ , 314. Calc.:  $M$ , 312).

Another sample of the chief solid acid was isolated from the acetone extract of a sample of latex crêpe rubber as follows: The mixture of the crystallisable substances which separated on allowing the extract, slightly diluted with acetone, to stand for several months was extracted with chloroform. The residue left on removal of the chloroform was separated by several crystallisations from alcohol and ethyl acetate into (a) a sterol ester (less soluble) and (b) a fatty acid (more soluble). The latter after several recrystallisations melted at 67—69° and had an equivalent weight of 295. It was purified further through its barium salt and then, after recrystallisation from acetone, aqueous acetic acid, and chloroform, had m. p. 68.5—69.5° (Found: equiv. by titration, 293, 289).

#### *The Liquid Fraction.*

This fraction was distilled with steam, which removed the last traces of acetone and also mesityl oxide, evidently formed from the acetone during the extraction. No essential oil was present. After removal of the non-volatile oil with ether, the aqueous layer contained a small amount of nitrogenous material precipitable by alkaloidal reagents; phosphomolybdic acid precipitated 2.5 g. (from 21.7 kg. of crêpe rubber) and in the case of slab crêpe, the precipitate given by platinic chloride contained 24.0% of platinum and did not melt at 295°. Both precipitates gave the pyrrole test on ignition.

The Liquid Fraction consisted preponderantly of unsaturated fatty acids, although some evidence was obtained of the presence of a magnesium salt. After steam distillation the fraction was esterified by hydrogen chloride in methyl alcohol at 0°, the ester mixture distilled, and the fraction, b. p. 195°/9 mm.—185°/5 mm., saponified. The free acid thus obtained had, after removal of a little crystalline material, a mean molecular weight (by titration) of 317 and an iodine absorption (Hübl) of 140, 141. *Hydrogenation.* 8.63 G. were treated with purified hydrogen in ether in presence of platinum-black carried on finely-divided barium sulphate. Unfortunately, some of the alkaline sodium hyposulphite solution over which the hydrogen was stored was sucked into the reaction flask, and in consequence only 619 c.c. of hydrogen were taken up

instead of the 1100 c.c. corresponding to the iodine value. Nevertheless, pure stearic acid was isolated in such good yield and so easily that it may be considered certain that only  $C_{18}$  unsaturated acids were present in the liquid submitted to hydrogenation. The crystals obtained after evaporation of the ether had m. p.  $68.5^{\circ}$  after recrystallisation from ethyl acetate and  $69-69.5^{\circ}$  after further recrystallisation from alcohol and from chloroform (Found : equiv., 281, 284). A total of 3.66 g. of stearic acid was isolated and the final mother-liquor left on evaporation 2.34 g. of impure stearic acid. *Oxidation.* The potassium soaps from 3 g. of the mixed acids were oxidised in aqueous solution with 3 g. of potassium permanganate. That part of the product which was soluble in cold ether was extracted with carbon tetrachloride. The portion thus extracted melted at  $60^{\circ}$  after recrystallisation, and was probably impure saturated acid. The portion (0.05 g.) unextracted by the carbon tetrachloride melted at  $124-126^{\circ}$ , had a molecular weight by titration of about 320, and was probably dihydroxystearic acid (*vide infra*). (A sample of dihydroxystearic acid prepared from Kahlbaum's oleic acid melted at  $128^{\circ}$  after several recrystallisations.) That part of the product which was insoluble in cold ether amounted, after recrystallisation from aqueous alcohol, to 0.42 g. and melted at  $160-170^{\circ}$ . By extracting it with boiling water, crystals were obtained, m. p.  $155-156^{\circ}$ , having an equivalent weight (by titration) of 356 and probably representing sativic acid. *Bromination.* A sample of the mixed acids was brominated in cold ethereal solution by Muggenthaler's method. No ether-insoluble bromide was obtained, and hence linolenic acid was absent. A small amount of a bromide melting, after recrystallisation from light petroleum, at  $112^{\circ}$  was obtained. (Linoleic acid tetrabromide melts at  $113-114^{\circ}$ .)

In order to identify the liquid acids with greater certainty, the solvent was removed from the acetone extract of 11 kg. of latex crêpe rubber, and the residue was boiled with water, in order to eliminate any mesityl oxide and to extract water-soluble constituents. The material was then boiled with 5% potassium hydroxide solution in excess of the amount equivalent to the acid known to be present in the rubber, and, after most of the material had gone into solution, the liquid was evaporated and distributed on pumice. This was then dried on a steam-bath and extracted with light petroleum, which removed, in addition to sterol and other unsaponifiable material, some potassium linoleate. This salt separated on cooling and after recrystallisation was obtained as a pale yellow powder (21 g.), which rapidly became brown in the air. Oxidation with potassium permanganate converted it



into sativic acid, insoluble in light petroleum or ether, melting at 165° after one recrystallisation from alcohol, and having an equivalent weight of 338 (sativic acid, 348). The pumice was now boiled with water and the acids liberated from the soap solution thus obtained were washed and dried [Found: *M* (mean), 340, 340. Iodine absorption, 144, 145%]. The potassium salts derived from 19 g. of the acids gave, on oxidation with permanganate: (a) 0.95 g., soluble in light petroleum, melting at 45–60° after two recrystallisations, and probably representing impure saturated acid; (b) 0.85 g. of dihydroxystearic acid (white crystals, m. p. 128–130°. Found: C, 67.8; H, 11.8%); (c) 2.7 g. of sativic acid. The last was separated by fractional crystallisation into portions, m. p. 169.5° and 154°, respectively. Nicolet and Cox (*J. Amer. Chem. Soc.*, 1922, **44**, 144) have shown that the two *dl*-mixtures of tetrahydroxystearic acids formed by the oxidation of linoleic acid can be separated by fractional crystallisation, the melting point of one being 171° and of the other 153°.

The zinc salt of a fatty acid was left on the pumice after the extraction of the soaps. It melted at 123°, and was probably impure zinc stearate derived from the zinc of the galvanised iron extractor and the stearic acid of the resin. A specimen of the zinc salt prepared from a somewhat impure sample of the solid acid isolated from the resin (m. p. 67–69°), by heating the acid in cymene solution with zinc oxide, melted at 123°.

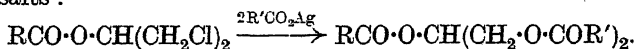
Hence the presence of oleic and linoleic acids in the Liquid Fraction can be regarded as established; and, since further only  $C_{18}$  acids are present, it seems safe to assume that the higher liquid fatty acids in rubber consist of oleic and linoleic acids exclusively. The purest sample of the mixed liquid fatty acids isolated showed an iodine absorption of 140 (*vide supra*). As this sample probably contained a small amount of solid acid as impurity, it is probable that the amount of linoleic acid present is considerably more than twice that of oleic acid. This conclusion is supported by the relative yields of dihydroxy- and tetrahydroxy-stearic acids obtained on oxidation.

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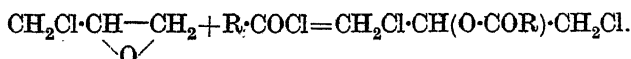
CXC.—*Some Fatty Acid Derivatives.*

By GEORGE STAFFORD WHITBY.

This paper describes the use of the silver salts of the fatty acids (which are obtainable by a convenient procedure described in the experimental part) for the preparation of derivatives such as the glycerides, acid anhydrides, and esters by double decomposition with appropriate halogen compounds. Certain mixed triglycerides have been prepared by treating  $\beta$ -acyl dichlorohydrins with such silver salts:



$\beta$ -Acyl dichlorohydrins can be prepared by the action of acyl chlorides not only on  $\alpha$ -dichlorohydrin, but also on epichlorohydrin: *i.e.*, acyl chlorides add on to epichlorohydrin in the same sense that hydrogen chloride does, the chlorine assuming the  $\alpha$ -position:



This has been shown to be the case for propionyl, butyryl, and stearyl chlorides.

The silver salts of the fatty acids react very easily with acyl chlorides, yielding acid anhydrides, and readily with alkyl halides, yielding esters. In a homologous series of esters of palmitic acid and in a similar series of esters of stearic acid, the melting point falls from the methyl ester to a minimum in the butyl ester.

Heintz (*Ann. Phys.*, 1852, **87**, 21, 267; 1854, **92**) concluded that the fatty acids derived from the saponification of spermaceti comprised stearic acid. The present author has isolated cetyl stearate from spermaceti by fractional crystallisation.

## EXPERIMENTAL.

*Silver Salts of Fatty Acids.*—Silver salts of both higher and lower fatty acids were obtained as fine, white powders, which suffered no discoloration when kept for 3 years in the light, by the following procedure: To a 2–4% alcoholic solution of the acid were added, in either order, 1 equiv. of aqueous ammonia (*d ca.* 0.9) and 1 equiv. of silver nitrate (dissolved in twice its weight of water; or dissolved in its own weight of water, and the warm solution diluted with alcohol). After 2–3 hours, the precipitate was filtered off, dried on a porous plate, powdered, and, if desired, dried at 50° for several hours. In the case of the higher fatty acids, the silver salt was precipitated in a more easily filterable form at about 50° than at room temperature. The yields were almost theoretical. Silver

stearate, palmitate, laurate, myristate, hexoate, butyrate, propionate, acetate, and oleate prepared by this procedure were shown to be pure by determining their silver content. The stearic acid used melted at  $69.5^{\circ}$ , and the palmitic acid at  $62.5^{\circ}$ .

From the higher fatty acids, silver salts were also obtained as white powders, stable in the light, by a modification of Krafft's method (*Ber.*, 1888, 21, 2266); the precipitates, however, were contaminated with a small amount (usually about 1%) of the free fatty acid, which could be removed by washing with alcohol or extraction with ether: Silver nitrate (1 equiv.) dissolved in a little water was treated with sufficient aqueous ammonia to re-dissolve the precipitate formed. The solution was added to an alcoholic solution of the fatty acid, precipitation completed by the addition of water, and the readily-filterable silver salt washed with alcohol and dried on a porous plate.

The solubility of silver palmitate and stearate in water at  $20^{\circ}$ , determined colorimetrically (Whitby, *Z. anorg. Chem.*, 1910, 67, 68), was 0.00123 g. and 0.00065 g., respectively, per litre. These two salts therefore fall in line with the silver salts of the lower acids, the solubilities of which change from member to member in a comparatively regular manner (Lieben, *Monatsh.*, 1884, 15, 404). Silver palmitate and stearate being less soluble than silver chloride, sodium chloride does not precipitate silver chloride from a solution of silver palmitate or stearate, held up by the minimum quantity of ammonia. Silver palmitate, being more soluble than silver stearate, requires less ammonia to cause it to dissolve in alcohol, and, conversely, it requires more water to precipitate it from ammoniacal alcoholic solution.

The silver salts of the higher fatty acids swell, disperse, and, on cooling, yield gels in various organic liquids, *e.g.*, aromatic hydrocarbons, on heating (compare Whitby, *Science*, 1921, 53, 580). Silver oleate yields gels more readily than does silver palmitate or stearate. Thus it gives a gel in benzene, whereas silver stearate requires the higher-boiling xylene to yield a firm gel; in toluene, it gives only a weak gel, and in benzene it merely swells. Silver oleate gives a weak gel in amyl alcohol. In *n*-propyl alcohol, it swells and disperses, but on cooling separates as flocks, not as a gel. Gelation in organic liquids can be obtained at a lower point in the fatty acid series in the case of the silver than in the case of the alkali salts. Thus, silver hexoate dissolves in hot xylene and on cooling the sol will set to a weak gel, whereas potassium and sodium hexoates remain undispersed in boiling xylene.

*β-Acyl Dichlorohydrins.*

The  $\alpha$ -dichlorohydrin used was prepared by the action of fuming hydrochloric acid on epichlorohydrin.

*β-Butyryl Dichlorohydrin.*—(a) A mixture of 29.58 g. of  $\alpha$ -dichlorohydrin and 23.72 g. of butyryl chloride was, after the initial reaction had subsided, warmed at 50° to complete the reaction, moisture being excluded (loss, 7.95 g. Calc., 7.82 g.). Distillation yielded a product, b. p. 223.5°, having a fruity odour,  $n_D^{20}$  1.4540,  $d_{20}^{20}$  1.1796, saponification number 843 (Calc. for  $C_7H_{12}O_2Cl_2$ , 845.5). (b) A mixture of 23.05 g. of epichlorohydrin and 29.05 g. of butyryl chloride (ca. 10% excess) was heated under reflux for 8 hours at 75°, the entry of moisture being prevented. The twice-distilled product had b. p. 223.5°,  $n_D^{20}$  1.4540,  $d_{20}^{20}$  1.1792, saponification number 841.5. Truchot (*Compt. rend.*, 1865, 61, 1170) gives b. p. 226°/738 mm. and  $d_4^{11}$  1.194.

*β-Propionyl dichlorohydrin* was prepared in similar ways to those mentioned above, except that in (b) the mixture of epichlorohydrin and propionyl chloride was heated in a sealed tube at 135° for 3 hours. The methods gave identical products, b. p. 208°,  $d_{20}^{20}$  1.2222.

*β-Palmityl Dichlorohydrin.*—Reaction between 13.79 g. (ca. 20% excess) of  $\alpha$ -dichlorohydrin and 22.15 g. of palmityl chloride was completed by heating the mixture for 1 hour in a boiling water-bath (loss, 2.93 g. Calc., 2.94). The product, which set solid on cooling, crystallised from alcohol in white crystals, m. p. 34.4°,  $n_D^{20}$  1.4527 [Found: saponification number, 456.7; Cl, 19.2 (by saponification), 19.1 (by Carius).  $C_{15}H_{30}O_2Cl_2$  requires Cl, 19.3%; saponification number, 458.7]. Palmitic acid isolated after saponification, 68.97 (calc., 69.76%).

*β-Stearyl Dichlorohydrin.*—(a) This was prepared from  $\alpha$ -dichlorohydrin and stearyl chloride in the manner described for the preparation of  $\beta$ -palmityl dichlorohydrin. It had m. p. 39.5° and  $n_D^{20}$  1.4528 (Found: saponification number, 424.1; Cl, 17.8.  $C_{21}H_{40}O_2Cl_2$  requires Cl, 17.85%; saponification number, 426.0). Stearic acid isolated after saponification, 72.18 (calc., 71.91%). (b) 20.8 G. of stearyl chloride were heated with 6.8 g. of epichlorohydrin in a sealed tube at 130° for 3½ hours. The product, on recrystallisation from alcohol, readily yielded pure  $\beta$ -stearyl dichlorohydrin. It contained a small amount of material of low melting point and very slight solubility in alcohol, the nature of which was not investigated.  $n_D^{20}$ , 1.4530. Saponification number, 423.

*Mixed Triglycerides.*

*β-Palmitodistearin* (*β-Palmityl αα'-distearyl glyceride*).—(a) Powdered *β*-palmityl dichlorohydrin (1 mol.) and silver stearate (2 mols.) were mixed and heated either for 3 hours at 155° or for 5 hours at 135°. An ethereal extract of the product slowly deposited the fat as a pale cream, microcrystalline solid, m. p. 63·5°, and 64·8° after recrystallisation from ether; the crystals from the mother-liquor had the same melting point.  $n_D^{20}$  1·4467. Mean dispersion ( $n_F - n_C$ ), 0·00788. Saponification number, 196·2 ( $C_{55}H_{106}O_6$  requires 195·2). 1·6269 G. of the mixed silver salts prepared, by the method described earlier, from the mixed fatty acids obtained on saponification gave 0·4595 g. of silver (calc., 0·4593 g.). Freedom of the product from stearic or palmitic acid was shown by the fact that addition of silver nitrate followed by ammonia to an alcoholic solution produced no precipitate. The fat was practically insoluble in cold alcohol.

(b) The glyceride was also prepared from *β*-palmityl dichlorohydrin and silver stearate, reacting in hot phenetole for 2½ hours. The filtrate, on cooling, deposited the fat as rosettes or sheaves of needles, m. p. 64°. After recrystallisation from ether, the product agreed in melting point and saponification number with that described above.

The m. p. of *β*-palmitodistearin is given as 63° by Kreis and Hafner (*Ber.*, 1903, 36, 2766) and Bömer and Limprick (*Z. Nahr. Genussm.*, 1913, 25, 354) and as 67·1° by Amberger and Bromig (*Biochem. Z.*, 1922, 130, 252).

*β-Stearodipalmitin* (*β-stearyl αα'-dipalmityl glyceride*) was prepared from *β*-stearyl dichlorohydrin and silver palmitate by method (a). M. p. 63·3° (Amberger and Bromig, *loc. cit.*, give 59·1°). Saponification number, 202·6 ( $C_{53}H_{102}O_6$  requires 201·8).

*β-Butyrodipalmitin* (*β-Butyryl αα'-dipalmityl glyceride*).—With the aid of some ether, silver palmitate (2 mols.) and *β*-butyryl dichlorohydrin (1 mol.) were mixed. The ether was removed by warming on the water-bath, and the mixture heated at 170° for ½ hour with occasional stirring. When cold, the product was extracted with ether, silver chloride filtered off, and the ether removed. The residue was dissolved in alcohol and treated with the quantity of alcoholic potassium hydroxide necessary to neutralise the free acid present. The alcohol was then removed at 40° under reduced pressure, the residue extracted with dry chloroform, the chloroform removed, and the product recrystallised from alcohol. It then had m. p. 43·6°,  $n_D^{20}$  1·4431,  $n_D^{25}$  1·4397,  $n_D^{30}$  1·4359; saponification number, 265·6 ( $C_{41}H_{74}O_6$  requires 263·3). 100 G. of absolute alcohol at 20° dissolve 0·55 g. of *β*-butyrodipalmitin.

*$\beta$ -Palmitodibutyryn* ( *$\beta$ -Palmityl  $\alpha\alpha'$ -dibutyryl glyceride*).—An intimate mixture of  $\beta$ -palmityl dichlorohydrin (1 mol.) and silver butyrate (2 mols.) was heated at 150° for 40 minutes, being stirred at intervals. The procedure used to isolate  $\beta$ -butyrodipalmitin was then followed. It was necessary to cool the alcoholic solution in ice in order to obtain crystals. These had m. p. 17°, and 18° after recrystallisation from alcohol.  $n_D^{20}$  1.4530. Saponification number, 388 ( $C_{27}H_{50}O_6$  requires 385.1).

#### *Acid Anhydrides.*

*Propionic Anhydride*.—Silver propionate (31.8 g.) and propionyl chloride (16.25 g.) developed considerable heat on mixing. No propionyl chloride came over on distillation. The yield of the crude anhydride was 20.0 g. (88%), and on redistillation this gave 80% of pure propionic anhydride, b. p. 165°.

*Butyric Anhydride*.—(a) From silver butyrate and butyryl chloride in the manner just described, a good yield of butyric anhydride, b. p. 193°, was obtained. (b) Lachowiz's method of preparing acetic and propionic anhydrides (*Ber.*, 1884, 17, 1218; 1885, 18, 2920) gave a poorer yield of butyric anhydride than method (a). A mixture of 40 c.c. of butyryl chloride and 600 g. of powdered lead nitrate (dried at 100°) was heated on the water-bath under reflux for 2–3 hours; it was then extracted with dry benzene, and the extract distilled. By several redistillations of the fraction b. p. 165–200°, a 50% yield of butyric anhydride was obtained.

*Palmitic Anhydride*.—A mixture of 6.40 g. of palmityl chloride and 8.19 g. of silver palmitate was heated and stirred on the water-bath for 10 minutes, and, when cold, was extracted with anhydrous ether. The product, recrystallised from ether, had m. p. 62.6°. Another sample had m. p. 63.0° after recrystallisation from benzene. Saponification number, 226; *M*, cryoscopic in benzene, 402 [ $(C_{15}H_{31}\cdot CO)_2O$  requires saponification number 226.8; *M*, 394]. 100 G. of absolute alcohol at 20° dissolve 0.18 g. of palmitic anhydride.

*Stearic Anhydride*.—This was prepared from stearyl chloride and silver stearate in a similar way to that just described. After recrystallisation from ether, the substance was obtained as large, shining plates, similar in appearance to stearic acid. M. p. 70.5°. Saponification number, 202.5; *M*, cryoscopic in benzene, 540 [ $(C_{17}H_{35}\cdot CO)_2O$  requires saponification number, 203.7; *M*, 550.7]. 100 G. of absolute alcohol at 20° dissolve 0.023 g. of stearic anhydride. The solubility in ether was clearly less than that of stearic acid.

The anhydrides of palmitic and stearic acids, although very similar to the corresponding acids in melting point and appearance, are much less soluble and have higher refractive indices. The following measurements were all made with the same instrument:

*Refractive indices of some fatty acids and their anhydrides.*

Propionic acid : $n_D^{17}$ 1.3874.	Propionic anhydride : $n_D^{17}$ 1.4041.
<i>n</i> -Butyric acid : $n_D^{18}$ 1.3990.	<i>n</i> -Butyric anhydride : $n_D^{18}$ 1.4143.
Palmitic acid : $n_D^{70}$ 1.4309.	Palmitic anhydride : $n_D^{70}$ 1.4359.
Stearic acid : $n_D^{80}$ 1.4300.	Stearic anhydride : $n_D^{80}$ 1.4362.

*Esters of Palmitic and Stearic Acids.*

*Cetyl Palmitate : Cetyl Stearate.*—These were prepared by heating a mixture of the appropriate silver salt (made from a sample of the pure acid) and recrystallised cetyl iodide (m. p. 21.9°) in a boiling water-bath for  $\frac{1}{2}$  hour, with stirring at intervals. The reaction mixture was extracted with ether, silver iodide filtered off, and the ethereal solution allowed to deposit crystals. The yields were practically theoretical, and the products, which consisted of lustrous, white plates, were so pure that recrystallisation from ether or glacial acetic acid failed to change the original melting point. Saponification numbers : cetyl palmitate, 117.0 ( $C_{15}H_{31} \cdot CO_2 \cdot C_{16}H_{33}$  requires 116.7); cetyl stearate, 111.1 ( $C_{17}H_{35} \cdot CO_2 \cdot C_{16}H_{33}$  requires 110.3). Both esters were readily soluble in acetone, carbon disulphide, or chloroform, and were very soluble in benzene. Ethereal solutions were occasionally supersaturated, but crystallisation was immediately induced by touching with ice a point in the vessel.

	Cetyl palmitate.	Cetyl stearate.
Melting point .....	51.6°	56.6°
$n_D^{80}$ , $n_D^{85}$ .....	1.4429, 1.4415	—
$n_D^{70}$ .....	1.4398	1.4410
100 G. of abs. ether dissolve at 22° .....	21.01 g.	9.08 g.
"    "    "    "    0° .....	2.30 g.	0.73 g.
"    "    alcohol    "    22° .....	0.0495 g.	0.0594 g.
"    glacial acetic acid dissolve at 22° ...	0.0633 g.	0.0388 g.
Turbidity temperature (Valenta test, with 2 c.c. of glacial acetic acid and 2 c.c. of ester) .....	109°	Turbid to b. p.

*Cetyl Stearate from Spermaceti.*—400 G. of a sample of spermaceti (m. p. 42–44°;  $n_D^{70}$  1.4397; turbidity temperature 77°; saponification number 125.8; iodine absorption 5.89%) were recrystallised from ether nineteen times; 2.2 g. were obtained of a product with a constant melting point of 56.6° and agreeing in saponification number, refractive index, and turbidity temperature with cetyl stearate. On the basis of determinations of the amount and melting point of the material in the mother-liquors from the successive

crystallisations, and of determinations of the melting point of artificial mixtures of cetyl palmitate and cetyl stearate, a rough estimate of the amount of cetyl stearate in the sample of spermaceti examined was made as 1.1%. A second sample of spermaceti was also examined. 1200 G. (original m. p. 41—44°) yielded, after ten crystallisations, 1.5 g. of crystals, m. p. 55.5°, having a saponification number of 111.5 (calc., 110.5) and giving cetyl alcohol (m. p. 50° after several recrystallisations from alcohol) and stearic acid (m. p. 65° after three recrystallisations from alcohol) on hydrolysis.

*Benzyl Palmitate*.—Equivalent quantities of silver palmitate and benzyl chloride were heated, with stirring at intervals, for  $\frac{1}{2}$  hour at 145°. The ester was extracted with ether and recrystallised from alcohol. M. p. 36° (compare Shonle and Row, *J. Amer. Chem. Soc.*, 1921, 43, 361).  $n_D^{20}$  1.4620. 100 G. of absolute alcohol at 16° dissolve 3.30 g.

*Benzyl stearate* was prepared similarly to benzyl palmitate. M. p. 44.3° (Shonle and Row, *loc. cit.*, give m. p. 45.8°),  $n_D^{20}$  1.4627. 100 G. of absolute alcohol at 16° dissolve 0.685 g.

*Homologous Series of Esters*.—The esters the physical constants of which are recorded in the following table were prepared from the appropriate silver salt and alkyl halide. In the case of methyl stearate, ethyl palmitate, and ethyl stearate a mixture of equivalent amounts of the silver salt and the alkyl iodide was gradually heated in xylene to 100° and maintained at that temperature for about 10 minutes. Silver iodide was filtered off, and washed with hot xylene. The xylene solution was, if necessary, concentrated under reduced pressure, the ester allowed to crystallise, and then recrystallised from alcohol to a constant melting point.

Palmitate.	M. p.	$n_D^{50}$ .	$n_D^{78}$ .	Saponification number.	
				Found.	Calc.
Ethyl .....	23.5°	1.4278	1.4200	204	197.3
n-Propyl .....	20.4	1.4290	1.4211	186	188.1
n-Butyl .....	16.9	1.4312	1.4232	179.5	179.7
n-Amyl .....	19.4	1.4320	1.4241	171	172
isoAmyl .....	12.5	1.4315	1.4236	175	172
n-Octyl .....	22.5	1.4358	1.4277	152	152.3
<b>Stearate.</b>					
Methyl .....	38.8				
Ethyl .....	33.6	1.4320	1.4238	182	179.5
n-Propyl .....	30.5	1.4323	1.4242	174	171.9
n-Butyl .....	27.5	1.4328	1.4250	165.9	164.8
n-Amyl .....	30	1.4342	1.4266	160	158.3
isoAmyl .....	23	1.4333	1.4260	160	158.3
n-Octyl .....	31.8	1.4373	1.4300	143	141.5

In the case of the other esters listed, with the exception of the cetyl esters, reaction was brought about by heating a mixture



of equivalent quantities of the silver salt and the alkyl iodide alone, without xylene, for  $1\frac{1}{2}$  hours at  $100^\circ$ . The product was extracted with hot alcohol. In the case of the octyl esters a mixture of the silver salt and octyl bromide was heated for  $2\frac{1}{2}$  hours at  $130$ – $140^\circ$ .

Both in the palmitate and in the stearate series the melting point reaches a minimum in the *n*-butyl esters, but the refractive index increases continuously.

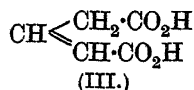
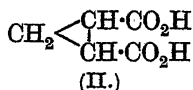
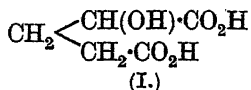
McGILL UNIVERSITY, MONTREAL.

[Received, February 22nd, 1926.]

CXCI.—*The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part VIII. Products derived from Pimelic Acid. An Application of Bischoff's Dynamic Hypothesis.*

By ALBERT HASSELL and CHRISTOPHER KELK INGOLD.

IN general, the action of alkalis on the  $\alpha$ -halogen derivatives of dibasic acids proceeds in three ways. Thus, monobromoglutaric acid yields a hydroxy-acid (I), a ring-acid (II), and an unsaturated acid (III), in addition to substances derived from the decomposition of these.

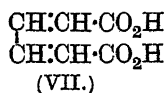
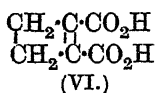
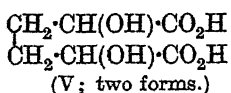
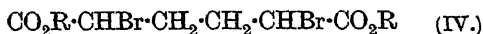


If the quantity of unsaturated acid formed is small, the reaction may be regarded as a competition between hydroxylation and ring-formation, and may be used to estimate the relative ease of ring-formation in the different cases. This method has been applied to a number of glutaric and adipic acids, with results explicable on the assumption that the volumes of groups attached to a central carbon atom determine the inclination of its valencies and the consequent tendency of that atom to participate in a ring of given type (Ingold, J., 1921, 119, 305, and later).

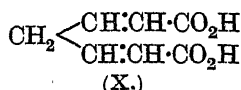
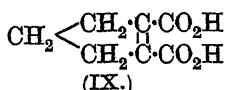
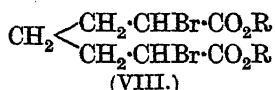
The halogen derivatives of pimelic acid have now been investigated, and, despite the fact that in this case there are difficulties in the way of a precise numerical comparison, the general results accord with the hypothesis. The ring formed is a five-membered one, and the ratio (ring-formation) : (hydroxylation) is much greater than in any case previously investigated.

In the case of the  $\alpha\alpha'$ -dihalogen-adipic esters (IV), concentrated

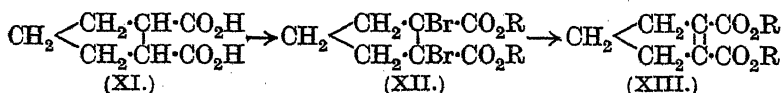
alkalis gave a small quantity of a *cyclobutene* acid (VI), and a considerable amount of muconic acid (VII) and of the hydroxy-acids (V).



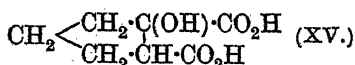
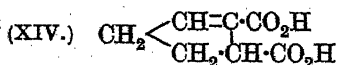
When  $\alpha\alpha'$ -dibromopimelic ester (VIII) was examined, a greatly increased tendency to ring formation was noticed. Under various conditions, a considerable proportion of the material was transformed into the *cyclopentene* acid (IX), although this acid did not always survive the conditions of its formation. When concentrated alkalis were employed, a second principal reaction gave rise to a doubly-unsaturated open-chain acid (X) (see below); the question as to whether this undergoes subsequent isomeric change is discussed below. So far as could be ascertained, dihydroxypimelic acids were not produced.



The constitution of the ring-acid (IX) follows from its identity with the acid synthesised by Haworth and Perkin (J., 1894, 65, 978) from the saturated *cyclopentane* acid (XI), the dibromo-ester (XII) of which, on treatment with potassium iodide, yielded the ester (XIII):

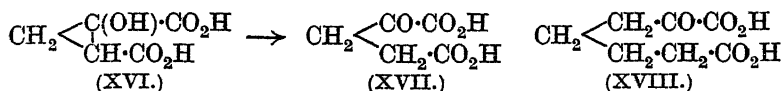


In the presence of concentrated alkalis, the unsaturated ring-acid (IX) undergoes change into the isomeric acid (XIV), the reaction being analogous to the conversion of citraconic acid into itaconic acid, and of  $\Delta^1$ -tetrahydrophthalic acid into the  $\Delta^2$ -acid. The change is not complete, and definite evidence of its reversibility has been obtained. At the same time, a small amount of the saturated hydroxy-ring acid (XV) is produced.

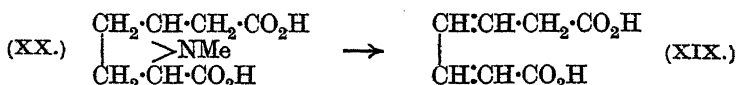


It is noteworthy that whereas the *cyclopropane* hydroxy-ring acid (XVI) is quantitatively converted into the isomeric ketoglutaric acid (XVII) by alkalis (Ingold, *loc. cit.*), the hydroxycyclopentane acid (XV) shows no tendency to pass into  $\alpha$ -ketopimelic acid

(XVIII). The two cases evidently represent the two limiting conditions of the keto-cyclol change.



Although formula (X) must represent the structure of the unsaturated open-chain acid initially produced from dibromopimelic ester, it is possible that this acid changes into the isomeride (XIX) under the conditions of the experiment. It is known that under these conditions  $\alpha\beta$ -unsaturated acids readily come into equilibrium with their  $\beta\gamma$ -unsaturated isomerides, and in this case the  $\beta\gamma$ -compound possesses a conjugated system from which it might be expected to derive sufficient stability to render the isomeric change practically non-reversible. The acid appears to be identical with the "piperylenedicarboxylic acid" obtained by Willstätter (*Ber.*, 1895, 28, 3287) by the exhaustive methylation of tropinic acid (XX):



These reactions do not, of course, prove the structure, but the tendency to the production of conjugated systems by the exhaustive methylation process is well known, and is illustrated by the exhaustive methylation of piperidine.

A remarkable reaction, which has not been observed in any of the shorter-chain series previously investigated, is that which leads to the formation of considerable quantities of the meso- and racemic forms of the dimethoxy-acid  $\text{CO}_2\text{H} \cdot \text{CH}(\text{OMe}) \cdot [\text{CH}_2]_3 \cdot \text{CH}(\text{OMe}) \cdot \text{CO}_2\text{H}$  when methyl-alcoholic potassium hydroxide is employed as the hydrolysing agent. Although the occurrence of this reaction creates difficulties when the attempt is made to extend to the pimelic acid series the method of numerical comparison previously employed, it is in accord with the view that the conditions governing all these reactions are essentially spatial; for whereas steric influences would prevent the accumulation of as many as four bulky groups ( $2\text{MeO}$  and  $2\text{CO}_2\text{H}$ ) in 1:5- and 1:6-positions, there is no obstacle in the way of their occupying 1:7-positions, and hence this reaction is not encountered in the glutaric and adipic acid series, and is met with for the first time in the pimelic acid series. It may be predicted that the occurrence of this reaction, under the conditions specified, will be found to be a peculiarity of the higher series, and that it will be prominent in the suberic and azelaic acid series.

## EXPERIMENTAL.

Pimelic acid was prepared by hydrolysis of the ethyl pentane-tetracarboxylate produced from ethyl sodiomalonate and  $\alpha$ -dibromopropane. It was dibrominated in the form of its chloride, and the dibromo-chloride converted into ethyl dibromopimelate, which was treated with 6*N*-methyl-alcoholic potassium hydroxide, as in the previous investigations of this series. The acid product, a pale yellow syrup, was dissolved in water, neutralised with ammonia, and a concentrated aqueous solution of lead acetate was added in four or five successive portions until no further precipitation occurred, the solutions being kept cold throughout. The various fractions of lead salt were collected separately and decomposed with a small excess of dilute sulphuric acid, the filtrates from the lead sulphate being concentrated in a vacuum and extracted with ether. The acid regenerated in this way from the first fraction of lead salt solidified almost completely, and some of the intermediate fractions, on being seeded with the solid and kept for some weeks, deposited crystals. These fractions were then again submitted to the fractional precipitation of lead salts, and some further crops of crystalline acid were thus obtained.

*Piperylenedicarboxylic Acid (XIX).*—The solid acid, after two crystallisations from ether, melted at 169° (Found : C, 53.7; H, 5.3.  $C_7H_8O_4$  requires C, 53.8; H, 5.1%), and corresponded closely in its properties with the acid obtained by Willstätter by exhaustive methylation of tropinic acid. The yield of purified material was 6.2% of the theoretical. The tetrabromide melted with decomposition at 217° (Found : Br, 67.0. Calc. : Br, 67.2%).

On oxidation with eight atoms of available oxygen in the form of 4% permanganate at the ordinary temperature, a small amount of malonic acid and much oxalic acid were obtained. On reduction by a large excess of sodium amalgam in boiling aqueous solution, a semi-solid product was obtained from which pimelic acid was isolated by draining and crystallisation from ether.

*cycloPentanol-1 : 2-dicarboxylic Acid (XV).*—The syrupy acids recovered from the lead salts, together with those obtained from the aqueous filtrates by extraction with ether after acidification, and desiccation over potassium hydroxide to remove acetic acid, were dissolved in ether and extracted with successive small quantities of water. The first extract, on evaporation in a vacuum, gave a residue which in course of time partly solidified. The remaining extracts gave syrups. The solid was drained (5.5% unpurified) and crystallised from acetone-benzene, from which it separated in small prisms, m. p. 159–160° (Found : C, 48.6; H, 5.8.  $C_7H_{10}O_5$  requires C, 48.2; H, 5.7%).

The *silver* salt was prepared from the neutral ammonium salt (Found: Ag, 55.5.  $C_7H_8O_5Ag_2$  requires Ag, 55.7%).

The *ethyl* ester was prepared by boiling the silver salt with ethyl iodide in ether solution; b. p. 168—171°/10—11 mm. (Found: C, 57.1; H, 7.8.  $C_{11}H_{18}O_5$  requires C, 57.4; H, 7.8%). On heating with acetic anhydride in a sealed tube at 180°, an oil was obtained which, on hydrolysis by hydrochloric acid, gave *cyclopentene-1:2-dicarboxylic acid*, m. p. 178°.

$\Delta^1$ -*cyclopentene-1:2-dicarboxylic Acid* (IX).—The syrupy residues from the ethereal and the various aqueous solutions obtained in the preceding separation were combined and esterified with ethyl alcohol and sulphuric acid. The esters, after several distillations, yielded a fraction, b. p. 146°/11 mm., which was hydrolysed by boiling with hydrochloric acid under a condenser sufficiently short to permit the escape of alcohol vapour. On evaporation of the aqueous solution, a solid product was obtained, which melted indefinitely at 140—150°, and after several crystallisations from water yielded a small quantity of the  $\Delta^1$ -*cyclopentene acid*, which was identified by analysis (Found: C, 53.9; H, 5.1. Calc.: C, 53.8; H, 5.1%) and by a mixed melting point determination.

$\Delta^2$ -*cyclopentene-1:2-dicarboxylic Acid* (XIV).—This acid appears to be the main constituent of the mixture, m. p. 140—150° (19% of the theoretical yield), but the separation of the last traces of the 178°-acid necessitates several alternate crystallisations from water and ethyl acetate. This acid is very much more soluble in water than the  $\Delta^1$ -isomeride; it separates from water or ethyl acetate in small prisms, m. p. 146—147° (Found: C, 53.5; H, 5.1.  $C_7H_8O_4$  requires C, 53.8; H, 5.1%).

*2:3-Dibromocyclopentane-1:2-dicarboxylic acid* was obtained when the  $\Delta^2$ -acid was exposed to bromine vapour for several days. The product, after being freed from bromine, was crystallised twice from glacial formic acid, from which it separated in small, dense prisms, which decompose with much frothing at 165° (Found: Br, 50.4.  $C_7H_8O_4Br_2$  requires Br, 50.6%).

On heating for a few minutes with boiling 64% aqueous potassium hydroxide, both the  $\Delta^1$ - and  $\Delta^2$ -*cyclopentene acids* yield a mixture consisting mainly of the  $\Delta^2$ -acid, along with a small amount of the  $\Delta^1$ -acid. In one experiment, starting with the  $\Delta^1$ -acid, a small amount of the hydroxy-ring acid was also isolated. The method of separation of these mixtures was substantially the same as that already described.

*Ethyl  $\alpha\alpha'$ -Dimethoxypimelate*.—In the distillation of esters (above) a large fraction (35% of the theoretical yield) was obtained, b. p. 160—175°/10 mm. This consisted essentially of a mixture of the

meso- and racemic forms of the dimethoxy-ester, and the central fraction, b. p. 166—169°/10 mm., gave correct figures on analysis (Found: C, 56·8; H, 8·7.  $C_{13}H_{24}O_6$  requires C, 56·5; H, 8·7%).

Both the central fraction and the main fraction (the former, b. p. 166—169°/10 mm., and the latter, b. p. 160—175°/10 mm.), on hydrolysis by means of hydrochloric acid, gave a syrupy acid which could not be induced to crystallise, although it yielded a silver salt having the correct silver content for the dimethoxy-compound (Found: Ag, 50·2.  $C_9H_{14}O_6Ag_2$  requires Ag, 49·8%). It was therefore digested with a small excess of pure thionyl chloride until sulphur dioxide ceased to be evolved, and after the excess of reagent had been removed at 100°, the acid chloride was treated with dry ammonia in ether solution. This process yielded a mixture of two crystalline amides.

The esters, b. p. 160—175°/10 mm., were mixed with concentrated aqueous ammonia (3 vols.), and the mixture was shaken frequently until it became homogeneous (3—6 days).

*αα'-Dimethoxypimelamide (A-form).*—This amide crystallised practically completely from the aqueous ammonia solution. It melted at 209—210°, and after one crystallisation from water was obtained pure, as prisms, m. p. 212°. The mixture of amides obtained from the ethereal ammonia solution yielded the A-amide in a pure condition after two crystallisations from water (Found: C, 49·2; H, 8·3.  $C_9H_{18}O_4N_2$  requires C, 49·5; H, 8·3%). The amide is readily soluble in hot water, sparingly soluble in cold, fairly easily soluble in methyl or ethyl alcohol or acetone, and almost insoluble in ethyl acetate, chloroform, or benzene.

*αα'-Dimethoxypimelamide (B-form).*—The ammonia solution from the esters, after the A-amide had been collected, was evaporated on the water-bath until, on cooling, it set to a stiff paste of crystals, which were drained on porous porcelain and crystallised from water and ethyl acetate; the compound separated in fluffy balls of minute needles, m. p. 167°. The aqueous solution from the decomposition of the acid chlorides, after the A-amide had been removed, was evaporated to dryness, and the residue extracted from the ammonium chloride with boiling ethyl acetate, from which, on concentration and cooling, the B-amide separated almost pure. It was crystallised from ethyl acetate (Found: C, 49·3; H, 8·2%). This amide is extremely soluble in hot water and very easily soluble in cold; it is fairly easily soluble in hot ethyl acetate, but almost insoluble in cold; it is easily soluble in acetone or methyl or ethyl alcohol, but insoluble in chloroform or benzene.

*αα'-Dimethoxypimelic Acid (A-form).*—A solution of the A-amide (1 g.) in 10 c.c. of concentrated sulphuric acid was treated between

0° and 5° with a strong aqueous solution of 0.6 g. of sodium nitrite delivered by a fine capillary tube dipping beneath the liquid, the addition occupying about 1.5 hours, during which the mixture was continually stirred. The solution was poured into water and extracted with ether, from which the A-acid was obtained as a clear gum (Found: C, 49.0; H, 7.3.  $C_9H_{16}O_6$  requires C, 49.1; H, 7.3%. Found for the *silver* salt: Ag, 49.6.  $C_9H_{14}O_6Ag_2$  requires Ag, 49.8%).

*αα'-Dimethoxypimelic Acid* (B-form).—This acid was prepared similarly from the B-amide and had similar properties (Found: C, 49.1; H, 7.4%. Found for the *silver* salt: Ag, 49.5%).

We desire to record our thanks to the Royal Society for a grant, with which part of the expense of this investigation has been met.

THE UNIVERSITY, LEEDS.

[Received, February 16th, 1926.]

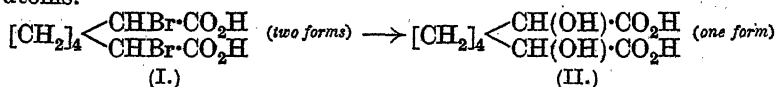
## CXCII.—*The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part IX. Products derived from Suberic and Azelaic Acids.*

By FRANK ROBERT GOSS and CHRISTOPHER KELK INGOLD.

ACCORDING to the hypothesis underlying this series of investigations, the action of concentrated methyl-alcoholic alkali on ethyl  $\alpha\alpha'$ -dibromosuberate should pursue a course similar to that observed in the pimelic acid series.

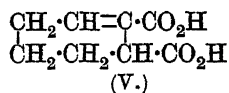
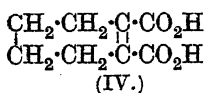
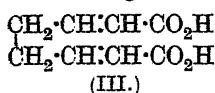
The bromination of suberic acid has been investigated by Gauthier, Hell, and Rempel (*Ber.*, 1882, 15, 149; 1885, 18, 814), who isolated a dibromo-acid of m. p. 173°.  $\alpha\alpha'$ -Dibromosuberic acid (I) should exist in meso- and racemic modifications, and a second form, m. p. 118–120°, has now been isolated. Both forms are produced together in the ordinary Hell-Volhard process of bromination, the less fusible acid in the greater quantity.

It appears impossible at present to assign configurations to these two acids, because, on treatment with dilute alkalis, both yield the same  $\alpha\alpha'$ -dihydroxysuberic acid (II), so that in one case or the other an inversion must occur at one of the two asymmetric carbon atoms.



By the action of alcoholic alkali on the less fusible dibromo-acid, Hell and Rempel (*loc. cit.*) obtained an acid,  $C_8H_{10}O_4$ , which

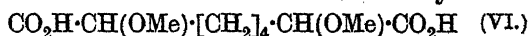
they termed "suberocolic acid," but they were unable to ascertain whether it was a doubly unsaturated open-chain acid (III) or a cyclohexene acid such as (IV). It has now been found that the acid has an open-chain structure, for, on partial reduction, it forms a dihydro-derivative which is still unsaturated, and on vigorous reduction gives suberic acid.



The acids (IV) and (V) are, however, produced along with (III) when ethyl dibromosuberate is treated with concentrated alkalis under the conditions described in the experimental part of this paper. It is probable that (IV) is the first product, although it changes into (V) to a large extent under the conditions employed in its formation.

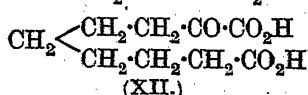
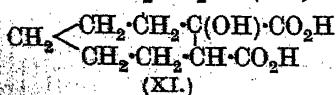
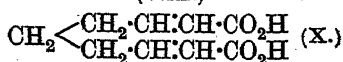
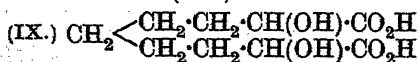
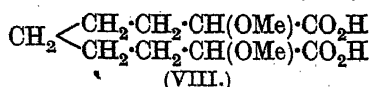
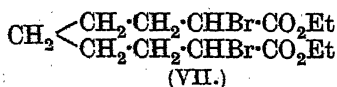
The cyclic acids had previously been prepared by the reduction of benzene derivatives, and Baeyer observed the conversion of (IV) into (V) by the action of alkalis (*Annalen*, 1890, 258, 209). He appears, however, to have regarded the change as complete, whereas, actually, the action is a balanced one, the acid (V) undergoing limited conversion into (IV) under identical experimental conditions.

When methyl-alcoholic alkali is used, considerable quantities of the meso- and racemic forms of the dimethoxy-acid



are produced in agreement with the prediction made in the preceding paper.

The general rules deduced in the preceding parts of this series suggest that the principal product of the action of concentrated methyl-alcoholic alkali on ethyl  $\alpha\alpha'$ -dibromoazelate (VII) should be the dimethoxy-acid (VIII) (in which the methoxyl groups occupy 1:9-positions) and that the by-products, if any, should consist of the dihydroxy-acid (IX) and the unsaturated acid (X). Further, it is not to be expected that cycloheptane ring closure would take place to any considerable extent, although some might occur, as in the cyclobutane series (Part II); an acid of constitution (XI) (if formed) might pass into its open-chain ketonic isomeride (XII).





The experiments now described show that under the conditions of hydrolysis which have been uniformly employed during these investigations the dibromo-ester (VII) is converted to the extent of at least 80% into a mixture of meso- and racemic methoxy-acids of formula (VIII) in striking agreement with the conclusions summarised in the preceding paper. Considerable difficulty was experienced in isolating the by-products of the reaction, but the dihydroxy-acid (IX) was obtained as a mixture of meso- and racemic isomerides, and an unsaturated acid, which may have been (X), was present. The production of the ring-acid (XI) could not be established with certainty, but an acid which appears to have the open-chain ketonic structure (XII) was isolated.

#### EXPERIMENTAL.

Suberic acid was prepared from castor oil, as described by Baker and Ingold (J., 1923, 123, 128).

*αα'-Dibromosuberic Acid (A-form).*—Suberic acid (60 g.) was warmed with 60 c.c. of thionyl chloride until sulphur dioxide ceased to be evolved, and the product treated on the steam-bath with 45 c.c. of bromine, added gradually to keep pace with the absorption. The product was poured into absolute formic acid and boiled until carbon monoxide ceased to be evolved; on cooling, 60 g. of the dibromo-acid, m. p. 160–170°, separated. After two crystallisations from water, this acid melted at 172–173° (Found: Br, 48.3. Calc.: Br, 48.2%).

*αα'-Dibromosuberic Acid (B-form).*—The formic acid mother-liquors were evaporated, and the pasty residue was drained on porous porcelain, and extracted with boiling chloroform until the m. p. of the undissolved portion rose above 160°. (This, after crystallisation from water, yielded a further 6 g. of the A-acid.) The residue from the chloroform solution was drained and crystallised several times from the same solvent; 20 g. of B-acid, m. p. 120–121°, were thus obtained (Found: Br, 48.0.  $C_8H_{12}O_4Br_2$  requires Br, 48.2%).

*Ethyl αα'-Dibromosuberate.*—Suberic acid (60 g.) was brominated as before, and the product poured into ethyl alcohol. The ester was extracted with ether after the addition of water, washed with dilute sodium carbonate solution, and distilled. It boiled constantly at 230°/31 mm., the yield being almost theoretical (Found: Br, 41.0.  $C_{12}H_{20}O_4Br_2$  requires Br, 41.2%).

*αα'-Dihydroxysuberic Acid.*—This substance is formed when either the A- or the B-form of αα'-dibromosuberic acid is boiled with 2N-aqueous sodium carbonate. The product, which is extracted with ether after acidification, is purified through the barium salt,

and thus obtained as a colourless gum which sets to a hard, crystalline mass, m. p. 166—168°, during the course of several months (Found: C, 46·8; H, 6·8.  $C_8H_{14}O_6$  requires C, 46·6; H, 6·8%).

*Suberocolic Acid*.—Ethyl  $\alpha\alpha'$ -dibromosuberate was treated with 6*N*-methyl-alcoholic potassium hydroxide under conditions comparable with those used in the previous investigations of this series. The cooled product was mixed with an equal volume of absolute ethyl alcohol, and the insoluble salts were collected, washed with ethyl alcohol, drained, dissolved in the minimal amount of water, and decomposed with concentrated hydrochloric acid. The sparingly soluble acid thus obtained was crystallised from boiling water (100 parts), from which it separated in branched needles, m. p. 253° (decomp.)—a considerably higher m. p. than that recorded by Hell and Rempel (Found: C, 56·5; H, 5·9. Calc.: C, 56·5; H, 5·9%). The yield was 11% of the theoretical.

*Oxidation of Suberocolic Acid*.—On oxidation with alkaline permanganate, suberocolic acid gives (as it should) succinic and oxalic acids, but not in the expected yields. In one experiment, 0·8 g., on treatment with 140 c.c. of 3% permanganate (7 atoms of available oxygen), gave 0·5 g. of calcium oxalate (theory, 1·2 g.) and 0·3 g. of succinic acid (theory, 0·55 g.).

*Reduction of Suberocolic Acid*.—The acid (0·5 g.) was reduced with 30 g. of 4% sodium amalgam on the steam-bath during 3 hours. After the mercury had been removed, the solution was acidified and extracted with much ether.

*Dihydrosuberocolic Acid (A-form)*.—The residue from the ether, after draining on porous porcelain, melted at 125—160°. After twice crystallising from water, small rosettes of needles were obtained, m. p. 170° (Found: C, 55·6; H, 7·0.  $C_8H_{12}O_4$  requires C, 55·8; H, 7·0%). The acid instantly decolorises cold alkaline permanganate, and on vigorous reduction (see below) yields suberic acid.

*Dihydrosuberocolic Acid (B-form)*.—This acid is formed along with suberic acid when suberocolic acid is reduced by boiling an aqueous solution with 50 g. of 4% sodium amalgam, added gradually during 4 hours. It separates from water in needles, m. p. 125° (Found: C, 55·7; H, 7·0%). The acid instantly decolorises cold alkaline permanganate, and on prolonged boiling with water and sodium amalgam yields suberic acid.

Suberic acid was separated from the B-form of dihydrosuberocolic acid by fractional crystallisation from hot water, and was identified by analysis (Found: C, 55·1; H, 8·0. Calc.: C, 55·2; H, 8·0%) and by comparison with a genuine specimen.

*$\Delta^2$ -cyclohexene-1:2-dicarboxylic Acid*.—The aqueous filtrate

from the suberocolic acid was extracted with ether, the residue obtained on evaporating the ether was rubbed with water, and the filtered solution evaporated in a vacuum. The residue obtained on evaporating the alcoholic solution with water was extracted with ether after acidification, and the residue from the concentrated and filtered ethereal solution was fractionally crystallised from ether. The combined residues were evaporated with water on the water-bath, and the crystals obtained after partial esterification of the residue were crystallised from water and identified by their properties, by analysis (Found: C, 56.3; H, 6.0. Calc.: C, 56.5; H, 5.9%), and by the m. p. of the anhydride (74°) prepared from them.

*Δ<sup>2</sup>-cycloHexene-1:2-dicarboxylic Acid*.—The acids separated by means of water contained this cyclohexene acid and suberocolic acid, which were separated by fractional crystallisation from water. The combined residues from the other ethereal and aqueous solutions were boiled with acetyl chloride for a short time, and the residue obtained by vacuum desiccation over potassium hydroxide was dissolved in ether and washed with sodium carbonate solution. The residue from the ether was dissolved in boiling water, from which the cyclohexene acid (4.7%) was obtained in a pure condition by evaporation and three crystallisations from water. It was identified by its properties, by analysis (Found: C, 56.4; H, 6.0. Calc.: C, 56.5; H, 5.9%), and by conversion into the anhydride of the *Δ<sup>1</sup>*-acid, as described by Baeyer (*loc. cit.*).

*αα'-Dimethoxysuberic Acid (A-form)*.—The sodium carbonate washings, on acidification and extraction with ether, yielded a mixture of acids which was separated into two fractions by boiling with ether. The sparingly soluble portion crystallised from a small amount of water in leaflets or rosettes of small needles (yield 20.4%), m. p. 145–146° (Found: C, 51.0; H, 7.6. C<sub>10</sub>H<sub>18</sub>O<sub>6</sub> requires C, 51.3; H, 7.7%).

*αα'-Dimethoxysuberic Acid (B-form)*.—On subjecting the more soluble fraction to repeated fractional crystallisation, from ether and water alternately, a further quantity of A-acid was obtained, whilst the B-acid became concentrated in the mother-liquors, partly on account of its greater solubility, and partly because of its much slower speed of crystallisation. It was finally obtained (2.8%) as rosettes of needles, m. p. 117–118° (Found: C, 51.7; H, 7.6%).

*Azelaic acid* was prepared by the oxidation of ricinoleic acid, as described by Baker and Ingold (J., 1923, 123, 128), and dibrominated in the form of its acid chloride. The dibromo-ester prepared from the dibromo-chloride was hydrolysed with 6*N*-methyl-alcoholic potassium hydroxide, as described in the earlier investigations of

this series. The acid product, a yellow syrup, was treated in various ways in the hope of inducing crystallisation, but without success, and it was therefore esterified with ethyl alcohol, and the ester carefully fractionated under reduced pressure, through a short column. After four distillations, the following fractions were obtained :

	(i).	(ii).	(iii).	(iv).	(v).	Residue.
B. p./30 mm. ...	198—205°	205—218°	218—221°	221—240°	240—260°	260°
Wt. (g.) ...	5.2	7.9	125.3	6.9	4.4	6.0
G./degree	0.7	0.6	41.8	0.4	0.2	—

*αα'-Dimethoxyazelaic Acid* (II).—The main fraction (iii), b. p. 218°/30 mm., on redistillation boiled mainly at 218—219°/30 mm. (Found: C, 58.9; H, 9.3. *Ethyl dimethoxyazelate*,  $C_{15}H_{28}O_6$ , requires C, 59.2; H, 9.2%). Both the main fraction and the central fraction gave on hydrolysis by hydrochloric acid a liquid mixture of the *meso*- and racemic forms of *αα'-dimethoxyazelaic acid* (Found: C, 52.8; H, 8.4.  $C_{11}H_{20}O_6$  requires C, 53.2; H, 8.0%), which, even after purification through the *silver* salt (Found: Ag, 46.5.  $C_{11}H_{18}O_6Ag_2$  requires Ag, 46.8%), could not be induced to solidify, and was therefore digested with thionyl chloride until sulphur dioxide ceased to be evolved. After the excess of thionyl chloride had been removed in a vacuum at 100°, the acid chloride was dissolved in ether and treated with dry ammonia; a crystalline precipitate, which, however, was a mixture of isomerides, was then obtained. Repeated crystallisation from water yielded one of the individuals in a pure condition as small plates, m. p. 164—165° (Found: C, 54.0; H, 8.6.  $C_{11}H_{22}O_4N_2$  requires C, 53.7; H, 8.8%). The same *αα'-dimethoxyazelamide* was obtained by digesting the ester with aqueous ammonia (*d* 0.880) for a month. Stellate clusters of crystals were formed which, after two crystallisations from water and one from ethyl acetate, gave small plates identical with the above. The more soluble isomeride could not be isolated in a pure condition: Crystals of the correct composition, having m. p. 143—146°, were obtained, but as in the course of numerous crystallisations small amounts of the amide, m. p. 164—165°, were obtained from them, they were concluded to be a difficultly separable mixture.

*αα'-Dihydroxyazelaic Acid* (III).—Fractions (iv) and (v) obtained in the above preparation were combined with corresponding fractions in three similar experiments and fractionally distilled four times. *Ethyl αα'-dihydroxyazelate*, b. p. 235—240°/16 mm., was thus obtained (3.7 g.) (Found: C, 56.9; H, 8.9.  $C_{13}H_{24}O_6$  requires C, 56.5; H, 8.7%). The *acid* obtained from it by hydrolysis with hydrochloric acid was a clear syrup which did not solidify, and from which no crystalline amide could be prepared (Found: C, 49.4; H, 7.7.

$C_9H_{16}O_6$  requires C, 49.1; H, 7.3%. Found for the *silver salt*: Ag, 49.7.  $C_9H_{14}O_6Ag_2$  requires Ag, 50.2%.

*$\alpha$ -Ketoazelaic Acid (VI).*—Fractions (i) and (ii) obtained in the preceding preparations gave on hydrolysis with mineral acids a syrupy acid which instantly decolorised cold alkaline permanganate, but the only crystalline products which could be obtained from it had not this property. Fractional distillation of the esters yielded no fraction of constant boiling point, and treatment with ammonia gave an impure mixture of amides from which only the dimethoxy-amide described above could be isolated. By hydrolysis of a fraction, b. p. 198—205°/23 mm., however, an acid was obtained which partly solidified after several months. On crystallisation from ether, rosettes of needles, m. p. 175°, were obtained (Found by micro-analysis: C, 53.5, 53.7; H, 7.1, 7.1.  $C_9H_{14}O_5$  requires C, 53.4; H, 7.0%). The amount obtained (0.05 g.) was insufficient for a detailed examination, but since the substance resembled  $\alpha$ -keto-glutaric acid in giving a dull reddish-brown colour with ferric chloride, it is believed to be  $\alpha$ -ketoazelaic acid, and not the isomeric hydroxycycloheptane acid.

We desire to record our thanks to the Royal Society for a grant with the aid of which some of the expense of this investigation has been defrayed.

THE UNIVERSITY, LEEDS.

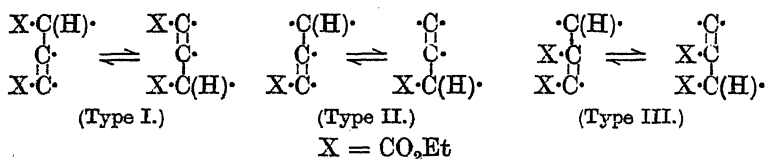
[Received, February 16th, 1926.]

### CXCIII.—*The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part I. The Three-carbon System.*

By CHRISTOPHER KELK INGOLD, CHARLES WILLIAM SHOPPEE, and JOCELYN FIELD THORPE.

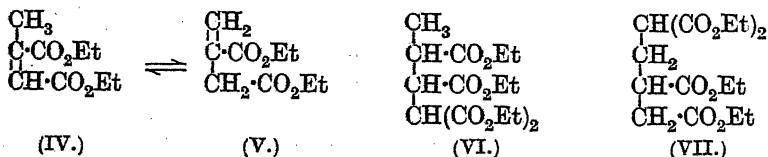
It has been shown (Birch, Kon, and Norris, J., 1923, **123**, 1361; Birch and Kon, *ibid.*, p. 2440; Kon and Linstead, J., 1925, **127**, 616, 815) that the mobility of the three-carbon system, which reaches a maximum in glutaconic esters (Type I), is also exhibited to a more limited degree in  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated esters (Type II), in which only one terminal carbethoxyl group is present, and in analogous unsaturated ketones and nitriles. This paper deals with the general question of the influence of substituents on tautomeric mobility, and includes a study of the case in which,

in addition to one terminal carboethoxyl group, a second carboethoxyl group is attached to the central atom of the three-carbon system (Type III).



A noteworthy contrast between systems (I) and (II) is that, whilst compounds of type (I) (glutaconic esters) usually attain equilibrium in the absence of an added reagent so that the isomeric forms cannot be isolated as distinct individuals, substances belonging to type (II) frequently require the addition of an alkaline catalyst, such as alcoholic sodium ethoxide, to bring about interconversion of the forms. Type III is found to resemble type II in this respect; on the other hand, there are important differences between these two types in the general character of the equilibria to which they attain.

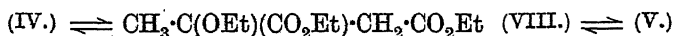
Citraconic and itaconic esters (IV and V) belong to type III, and they can, of course, be obtained as distinct individuals. There are, however, definite indications of their interconvertibility in the presence of alcoholic sodium ethoxide. Thus Hope found (J., 1912, 101, 894) that if citraconic ester were treated with ethyl sodiomalonate in ether or benzene, the normal addition compound (VI) was formed; whereas if he used alcohol as solvent, an isomeric ester (VII) was obtained, which could also be prepared directly from itaconic ester.



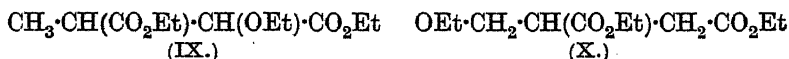
A re-examination of this reaction has shown that *both* the ester (VI) and its isomeride (VII) are formed from either citraconic or itaconic ester under a considerable variety of conditions, *e.g.*, by treatment with an equivalent or a large excess of sodium ethoxide in cold or in hot ethyl alcohol, or with sodium in boiling benzene. Under other conditions, only one isomeride could actually be isolated in the pure condition, the formation of the other being established by the production of derivatives.

These experiments, a fuller account of which is given below,

strongly emphasise the suggestion that citraconic and itaconic esters are tautomeric in the presence of sodium ethoxide, just as are the esters (and nitriles, etc.) of type II previously discussed. Hope, however, advanced the opinion that the interconversion in the presence of sodium ethoxide might take place through the adding on and splitting off of alcohol in accordance with the following scheme, and he succeeded in isolating an ethoxy-derivative to which formula (VIII) was assigned.

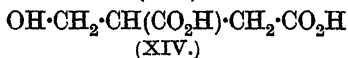
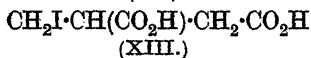
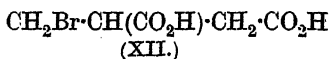
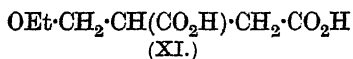


This view has, of course, the same mechanical simplicity as other "adding on and splitting off" theories of isomeric change, and it is necessary to explain why we regarded it as improbable. First it has been shown (E. H. Ingold, J., 1925, 127, 469) that although, in reversible addition reactions, fission corresponding with addition in the direction favoured by polar influences is in general readily effected, yet fission corresponding with addition in a non-favoured direction takes place with difficulty or not at all. The conversion of (VIII) into (V), involving as it does the removal of a  $\beta$ -ethoxyl group along with an  $\alpha$ -hydrogen atom, would be a fission of the latter class, and would certainly not take place under the experimental conditions employed. Secondly, in all alcohol-additions to unsaturated esters, the ethoxyl group takes up the same position as does the  $-CH(CO_2Et)_2$  group in the corresponding additions of ethyl malonate. Hence, regarding the malonic ester addition products (VI) and (VII) as derived from (IV) and (V), respectively, we see that if citraconic ester formed an ethoxy-compound it should have formula (IX), whilst if itaconic ester gave one it should have formula (X); and either of these on losing alcohol would, of course, pass back into the ester from which it was derived. Thus, not only would an ester of constitution (VIII) not be formed, but, even if it were, it would not undergo the changes which it was invented to explain.



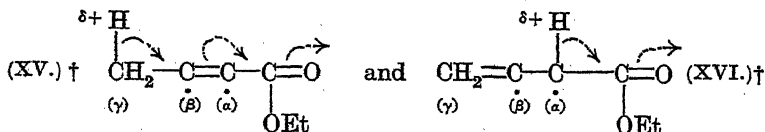
Proof that Hope's ethoxy-ester has in reality formula (X) was obtained by converting the corresponding ethoxy-acid (XI) with hydrobromic and hydriodic acids into the bromo-acid (XII) and the iodo-acid (XIII), respectively, and into the lactone (paraconic acid) of the hydroxy-acid (XIV), all of which were identified by comparison with specimens synthesised for the purpose. The isomeric bromo- and hydroxy-acids corresponding with the ethoxy-esters (VIII) and (IX) are known and their m. p.'s and properties

are such that they could not be confused with the substances obtained.\*



Thus, there is no evidence that an ethoxy-ester intervenes in the conversion of citraconic ester into itaconic ester; on the contrary, itaconic ester obviously must intervene in the conversion of citraconic ester into the ethoxy-ester obtained; and, naturally, the same ethoxy-ester can be obtained from itaconic ester directly.

Our view of the effect of sodium ethoxide and other alkaline reagents in promoting the interconversion of these and the other three-carbon tautomerides is best made clear by reference to a recent paper by Holmes and Ingold (this vol., p. 1305), in which it is shown that a hydrogen atom attached to a hydrocarbon radical may be extracted in the form of its ion (that is, the nucleus only) by the action of a powerful negative ion such as hydroxyl, and that this process is facilitated if the hydrogen atom is already in a state of *incipient* ionisation owing to the presence in the molecule of a group (electron-sink) which exerts a pull on the electrons involved in binding the hydrogen atom. Now the carbethoxyl group, like all groups which are *m*-directive in aromatic substitution, is regarded as a powerful electron-sink (compare Allen, Oxford, Robinson, and Smith, this vol., p. 401; Ingold and Ingold, *ibid.*, p. 1310), and hence the "mobile hydrogen atom" in citraconic and itaconic ester, and in similar pairs of three-carbon tautomerides, may be assumed to be in a state of incipient ionisation owing to small electron displacements in the directions



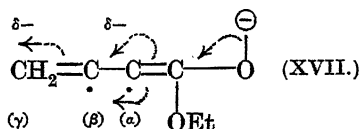
The former scheme is precisely similar to that given by Ingold and Ingold for *m*-substitution in the benzene ring (*loc. cit.*, Case 2, p. 1312). The conditions under which the isomeric change may occur will now depend entirely on the extent to which this preliminary loosening of the potential hydrogen ion has taken place.

\* Dr. Hope, to whom these data were privately communicated, is in complete agreement with the structural conclusions.

† For explanation of symbols, see Ingold and Ingold, *loc. cit.*, p. 1312, footnote.



If incipient ionisation is considerable, mere loose combination with neutral solvent molecules (ordinary hydrion solvation) will be sufficient to draw the hydrogen nucleus away. If, on the other hand, it is slight, the more powerful attraction of a negative ion will be required to effect removal, and it is in this way, we believe, that sodium ethoxide, a source of negative ethoxyl ions, acts in facilitating the interconversion of three-carbon tautomerides. As the hydrogen nucleus is drawn away, so the electron displacements, originally minute, are enabled to progress in the sense of formulæ (XV) and (XVI), until, when ionic dissociation is complete, the displacement also is complete, the negative ionic charge appearing on the oxygen atom; thus (XV) and (XVI) give the common ion (XVII).



The second half of the process, the recombination of the negative ion (XVII) with hydrion, is similarly comparable with *op*-substitution, the ion (XVII) corresponding in structure with a phenoxide ion (*loc. cit.*, Case I, p. 1312). In each of these ions there is assumed to be a weak tendency towards a return of the electrons, giving (in different electromeric phases) small negative charges in the  $\alpha$ - and  $\gamma$ - (or *o*- and *p*-) positions, to which, therefore, either positive ions, or the positive ends of incipiently ionised molecules, become attracted. In the case now under consideration, the positive ions would be solvated hydrions, and as combination proceeds, so the electrons would be drawn back in the sense of formula (XVII) until either the neutral molecule (XV) or its isomeride (XVI) is regenerated (compare with diazo-coupling).<sup>\*</sup> Or, an incipiently ionised molecule, such as water or alcohol, may be attracted, and the positive end of it (hydrogen) transferred to the three-carbon system by reaction in a cycle (compare with *op*-nitration, *loc. cit.*).

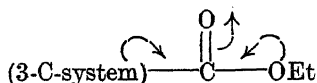
This view of activation in tautomeric change represents a rational development of principles previously formulated by E. H. Ingold (*Chem. and Ind.*, 1923, 42, 1246),<sup>†</sup> and we would apply it not only

<sup>\*</sup> The hydrions will, of course, also approach and combine with the negatively charged oxygen atom, but this produces no new isolable isomeride and is easily reversible (ordinary ionic dissociation). It is the circumstance that, when the hydrion approaches  $C_\alpha$  or  $C_\gamma$  the electrons return along the chain to that point and so *bind* the hydrion, which (according to this view) gives to the  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated isomerides their stability as individuals.

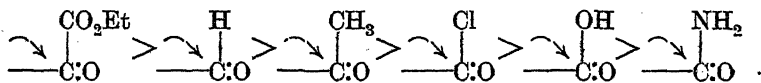
<sup>†</sup> Read to Section B of the British Association at Liverpool, September, 1923.

to three-carbon tautomerism, but also, with appropriate modifications, to all other mobile-hydrogen tautomeric systems, including ring-chain systems. Illustrations of its applications are, however, now confined to certain effects of structure on three-carbon tautomerism.

The effect of the terminal groups on the *mobility* of the three-carbon system (compare *inter alia*, Ingold and Piggott, J., 1922, 121, 2381; Birch, Kon, and Norris, *loc. cit.*) may readily be correlated with directive action in benzene substitution. Thus the smaller mobility of systems terminated by a carbethoxyl or carbonyl group, as compared with similar systems terminated by an acetyl group, is regarded as due to the competition :



This is only a particular case of the general principle that the greater the electron-giving tendency possessed by a group R (as indicated by its *op*-directive power in aromatic substitution) the smaller will be the mobility of a three-carbon system terminated by  $\cdot\text{CO}\cdot\text{R}$ . Thus the sequence  $\text{NH}_2 > \text{OH} > \text{Cl} > \text{CH}_3 > \text{H} > \text{CO}_2\text{Et}$  for *op*-directive power leads to the sequence

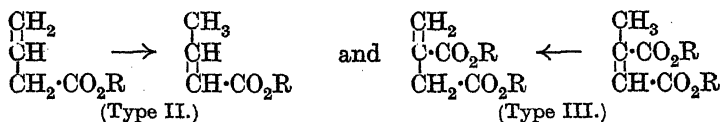


for the enhancement of three-carbon mobility. Similar series apply to related phenomena discussed by E. H. Ingold (*loc. cit.*) and, in passing, it may be noticed that the difference  $-\text{CO}\cdot\text{Cl} > -\text{CO}\cdot\text{OH}$  is utilised in the Hell-Volhard method of brominating aliphatic acids through their chlorides. The reason for the greater mobility of three-carbon systems in which there are two terminal carbethoxyl groups (glutaconic esters, type I) as compared with those in which there is only one (types II and III) is too obvious to require elaboration.

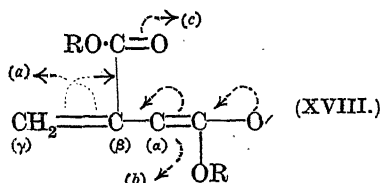
A general discussion of the effect of groups on the three-carbon *equilibrium* would necessarily be lengthy, but the method of treatment can be illustrated by means of a few examples. In the simple case of a three-carbon system activated by one terminal group, say a carboxyl group, six types of modification by substitution are possible, since either an *op*-directive group (electron source) or a *m*-directive group (electron-sink) might be introduced into either the  $\alpha$ -, or the  $\beta$ -, or the  $\gamma$ -position.

As illustration, we may consider the introduction of an electron sink into the  $\beta$ -position, the effect of which is to displace the

equilibrium in the direction favouring the  $\beta\gamma$ -unsaturated isomeride. For example, the isomeric changes



form a striking contrast (compare also Baeyer, *Annalen*, 1890, 258, 165; Hassell and Ingold, this vol., p. 1465; Goss and Ingold, *ibid.*, p. 1471). The reason for this effect is clearly seen if we consider the return of the electrons in the ion (XVII). Two routes are originally open, (a) and (b) (XVIII), but one of these (a) clashes with path (c) provided by the  $\beta$ -group; hence the hydrogen ion combines preferentially at the  $\alpha$ -carbon atom:



Similarly, in aromatic substitution, the introduction of a *m*-directing group in the *m*-position to a powerful *op*-directing group tends to facilitate substitution in the position *between* the two groups.

Again, the introduction of an *op*-directing group (electron source) in the  $\gamma$ -position will oppose (a), and in the absence of disturbing factors should therefore favour the  $\beta\gamma$ -unsaturated isomeride.  $\gamma$ -Alkyl groups are known to have this effect (compare *inter alia*, Wallach, *Annalen*, 1912, 394, 376; Beesley, Ingold, and Thorpe, J., 1915, 107, 1080; Birch, Kon, and Norris, *loc. cit.*; Kon and Linstead, *loc. cit.*). Analogous considerations may be applied to other cases, and the comparison with aromatic substitution obviously gives great scope for the prediction of the relative magnitude as well as the direction of the effect to be expected from different substitutions in different positions.

The analogy between tautomerism and reversible additive reactions has been emphasised in a number of recent memoirs, and a discussion of the application of these views to that subject will be given in an ensuing paper.

#### EXPERIMENTAL.

Citraconic anhydride was obtained (3 kg.) from citric acid, and the fraction, b. p. 204–205°/760 mm., esterified as described by Hope. It is important to distil the anhydride under ordinary

pressure to isomerise any itaconic anhydride. The ethyl citraconate had b. p. 118—120°/20 mm. (yield, 80%). Ethyl itaconate, b. p. 119—120°/20 mm., was prepared from itaconic acid.

*Addition of Ethyl Sodiomalonate to Ethyl Citraconate and Ethyl Itaconate and Separation of the Products.*—Ethyl sodiomalonate was prepared in the usual manner, with ethyl alcohol as solvent and the theoretical quantity of sodium, and the ethyl citraconate (1 mol.) added, the temperature being kept at 15°. After 24 hours, the pale yellow product was poured into water, and the product extracted with ether and washed with sodium carbonate. The residue obtained on evaporation of the ether was subjected to a long series of fractional distillations, as a result of which it was partly separated into two products: (a) b. p. 198—199°/10 mm., and (b) b. p. 190—191°/10 mm. The former (a) was ethyl *n*-butane- $\alpha\beta\delta$ -tetracarboxylate, since on hydrolysis by hydrochloric acid it gave *n*-butane- $\alpha\beta\delta$ -tricarboxylic acid, m. p. 121°, which was identified by comparison with a specimen prepared by hydrolysing the product of condensing ethyl sodioethanetricarboxylate with ethyl  $\beta$ -iodopropionate. The fraction (b) consisted of ethyl *n*-butane- $\alpha\beta\gamma$ -tetracarboxylate, since on hydrolysis it gave *trans*- $\alpha$ -methyltricarballic acid, m. p. 185°.

In view of the unsatisfactory character of this separation, the crude product obtained from the condensation of 525 g. of citraconic ester and 455 g. of ethyl malonate was treated in the following manner. An ethereal solution was shaken with 2*N*-aqueous sodium hydroxide and then mixed with 100 c.c. of ice-water and 50 c.c. of 50% potassium hydroxide. This alkaline solution was extracted twice with ether, the combined ethereal extracts were evaporated, and the residue was fractionally distilled. A first fraction (8 g.) had b. p. 140—180°/12 mm., and the main fraction (22 g.) b. p. 180—192°/12 mm.; on redistillation, this gave a colourless oil (20 g.), b. p. 189—190°/11 mm., consisting of ethyl *n*-butane- $\alpha\beta\gamma$ -tetracarboxylate (Found: C, 55.5; H, 7.5. Calc.: C, 55.5; H, 7.5%), since it yielded *n*-butane- $\alpha\beta\gamma$ -tricarboxylic acid on hydrolysis. The potassium hydroxide solution was acidified and extracted with ether, and the extract washed thoroughly with saturated aqueous sodium hydrogen carbonate. On evaporation of the extract, an oil (15 g.) was obtained, which on distillation gave a fraction (6.5 g.), b. p. 205—210°/15 mm., consisting of ethyl cyclopentan-3-one-1:2:4-tricarboxylate. On boiling this with hydrochloric acid for one hour and evaporating the solution, cyclopentanone-3-carboxylic acid, m. p. 62—64°, b. p. 170—174°/17 mm., was obtained. The more volatile ester fraction (5 g.), b. p. below 200°/15 mm., contained the ethyl cyclopentanonedicarboxylate and

ethyl *cyclopentanone*carboxylate described below. The sodium hydrogen carbonate solution was acidified with hydrochloric acid and extracted with ether, and the residue (60 g.) from the extract esterified with ethyl alcohol and sulphuric acid in the usual manner. An ethereal solution of the esters so obtained was washed with aqueous sodium hydrogen carbonate and then with aqueous potassium hydroxide at 0°. The ester (20 g.) on fractional distillation gave 12 g. of an oil, b. p. 200—204°/12 mm., consisting of ethyl *n*-butane- $\alpha\beta\delta\delta$ -tetracarboxylate (Found: C, 54.7; N, 7.4. Calc.: C, 55.5; H, 7.5%), since on hydrolysis only *n*-butane- $\alpha\beta\delta$ -tricarboxylic acid was obtained. The sodium hydroxide solution was acidified with hydrochloric acid and extracted with ether, and the extract washed with aqueous sodium hydrogen carbonate and then with ice-cold 10% aqueous potassium hydroxide. The ether extract on evaporation gave a resin. The potassium hydroxide solution was acidified and extracted with ether; ethyl *cyclopentanone*-1:2:4-tricarboxylate was then obtained. The sodium hydrogen carbonate solution was reacidified with hydrochloric acid, and the product obtained on extraction with ether was esterified with alcohol and sulphuric acid. The esters, after being washed in ethereal solution with aqueous sodium hydroxide and distilled, yielded, in addition to a small amount of substance, b. p. below 140°, a main fraction, b. p. 210—245°/12 mm., consisting essentially of ethyl dicarboxy*cyclopentenyl*malonate (see below). The sodium hydroxide solution was treated at 0° with excess of carbon dioxide, and the oil thus precipitated was extracted with ether. The residue from the ether on distillation gave a small fraction, b. p. below 145°/12 mm., and a main fraction, b. p. 145—154°/12 mm., consisting of ethyl *cyclopentanone*dicarboxylate (see below). The carbonated solution was rendered acid, and the product extracted with ether and re-esterified with alcohol and sulphuric acid. The esters so obtained, after being washed in ethereal solution with alkali and distilled, gave principally a fraction, b. p. 230—240°/12 mm., consisting mainly of ethyl dicarboxy*cyclopentenyl*malonate.

The various "low" fractions mentioned in the course of the foregoing account were combined and examined. They consisted principally of unaltered ethyl malonate, ethyl mesaconate, and ethyl itaconate, a possible indication of the reversibility of the reaction.

The same nine substances, namely, ethyl malonate, itaconate, mesaconate, butane- $\alpha\alpha\beta\gamma$ -tetracarboxylate, butane- $\alpha\beta\delta\delta$ -tetracarboxylate, *cyclopentanone*-mono-, -di-, and -tri-carboxylate, and dicarboxy*cyclopentenyl*malonate, were obtained, by the same method of separation, when the original condensation was carried

out at 80°, and also when ethyl itaconate was substituted for ethyl citraconate in either experiment. Similar condensations carried out with itaconic and with citraconic ester, both at 15° and at 80°, with the difference that the quantity of sodium employed was twice the theoretical, yielded the same products, together with a pale yellow mixture of sodium compounds the nature of which has not yet been elucidated. Other condensations were carried out in boiling benzene as the solvent, the ethyl sodiomalonate being prepared from "molecular" sodium and ethyl malonate. When ethyl citraconate was used, not only ethyl butane- $\alpha\beta\gamma$ -tetracarboxylate, but also  $\alpha\beta\delta\delta$ -tetracarboxylate and the *cyclopentane*-esters were obtained. The use of excess of sodium made no difference to these results, and the yellow sodium compounds were not obtained as when alcohol was used as solvent. Other condensations were effected by the aid of molecular sodium (1 mol.) in dry ether. In this case, using ethyl citraconate, ethyl butane- $\alpha\beta\gamma$ -tetracarboxylate was obtained in 80% yield, and the  $\alpha\beta\delta\delta$ -ester was not isolated; but it must have intervened in the production of ethyl *cyclopentanone*-tetracarboxylate, which was identified by hydrolysis to *cyclopentane*-3-carboxylic acid, m. p. 62°. The use of excess of sodium did not affect this result. Similar experiments using ethyl itaconate in place of ethyl citraconate led to 65–75% yields of ethyl *n*-butane- $\alpha\beta\delta\delta$ -tetracarboxylate, which was identified through its amide (m. p. 255°; compare Michael and Schulthess, *J. pr. Chem.*, 1892, 45, 57) and hydrolysis product. The *cyclopentane* esters were also obtained, but ethyl *n*-butane- $\alpha\beta\gamma$ -tetracarboxylate could not be identified. The presence of excess of sodium did not affect this result.

It appears, therefore, that the mobility of the unsaturated esters is less in benzene and ether than in alcoholic sodium ethoxide, and that in ether particularly, possibly on account of its low b. p., there is very little interchange.

The following compounds are new.

*Ethyl cyclopentanone*-3-carboxylate is a colourless oil, b. p. 109–111°/10 mm. It gives no colour with ferric chloride (Found: C, 61.4; H, 7.7.  $C_8H_{12}O_3$  requires C, 61.5; H, 7.7%). The *semicarbazone* was prepared by means of semicarbazide acetate and crystallised from ethyl alcohol in needles, m. p. 153.5° (Found: C, 50.6; H, 7.2.  $C_9H_{15}O_3N_3$  requires C, 50.7; H, 7.0%). The ester can be prepared by way of the acid chloride, which is obtained when phosphorus pentachloride acts on *cyclopentanone*-3-carboxylic acid.

*Ethyl cyclopentanone*-2:4 (or 2:3)-dicarboxylate has b. p. 150°/10 mm. and 160°/18 mm. It gives a deep red colour with ferric chloride (Found: C, 57.6; H, 7.3.  $C_{11}H_{20}O_5$  requires C, 57.8;

H, 7.0%). A semicarbazide could not be prepared. On hydrolysing the ester with hydrochloric acid, cyclopentanonecarboxylic acid, m. p.  $64^{\circ}$ , was obtained.

*Ethyl 2:4 (or 2:3)-Dicarboxycyclopentenylmalonate (or Ethyl 2:4 [or 2:3]-dicarboxycyclopentylidenemalonate).*—A number of crude specimens of this ester (51 g.) were combined and carefully distilled; 43 g. of a pure fraction, b. p.  $240\text{--}245^{\circ}/16\text{ mm.}$ , were then obtained (Found: C, 58.3; H, 7.1.  $\text{C}_{18}\text{H}_{26}\text{O}_8$  requires C, 58.3; H, 7.1%). The ester was unsaturated and gave no colour with ferric chloride. It showed an exaltation of refractivity of 1.9 units for sodium light ( $n_D^{20}$  1.46719;  $d$  1.13273). The acid obtained on hydrolysis was a syrup, and may have been a mixture of the endocyclic and exocyclic unsaturated acids, since the parent ester would almost certainly be tautomeric. From the first fractions obtained in the distillation of the above ester, a semicarbazone was obtained which was identified with that described above, m. p.  $153.5^{\circ}$ .

*Formation and Constitution of Ethyl  $\omega$ -Ethoxymethylsuccinate.*—This ester may be prepared either from citraconic ester, as described by Hope, or from itaconic ester. Using Hope's method, we found some difficulty in obtaining the ethoxy-ester free from unsaturated esters, but after a series of careful fractionations, about 15–20% of an ester, b. p.  $137\text{--}140^{\circ}/23\text{ mm.}$ , was obtained which decolorised permanganate only slowly. It gave correct figures on analysis and on treatment with aqueous ammonia yielded  $\omega$ -ethoxymethylsuccinamide, which was isolated by evaporating the ammonia solution in a vacuum and crystallising the residue from water. Thus obtained, the amide formed prisms, m. p.  $149\text{--}150^{\circ}$  (Found: C, 48.4; H, 7.8.  $\text{C}_7\text{H}_{14}\text{O}_3\text{N}_2$  requires C, 48.3; H, 8.0%). By the use of itaconic ester (20 g.), sodium (0.16 g.), and alcohol (96 c.c.), and by keeping the mixture at the ordinary temperature overnight, a product was obtained which, after four fractional distillations, yielded 3 g. of an unsaturated ester, b. p.  $130\text{--}135^{\circ}/23\text{ mm.}$ , and 5 g. of an ester, b. p.  $137\text{--}140^{\circ}/23\text{ mm.}$ , which only slowly decolorised alkaline permanganate. The unsaturated ester, on treatment with ammonia, was converted into mesaconamide, m. p.  $176\text{--}177^{\circ}$  (Found: C, 47.0; H, 6.3. Calc.: C, 46.9; H, 6.2%) and must therefore have consisted largely of mesaconic ester. The saturated ester was evidently the same ethoxy-ester as that obtained from citraconic ester, since it gave the same amide, m. p.  $149\text{--}150^{\circ}$ , on treatment with ammonia and the same acid on hydrolysis (Found: C, 56.6; H, 8.6. Calc.: C, 56.9; H, 8.6%). The ethoxy-acid obtained on hydrolysis had the m. p. and properties described by Hope.

*$\alpha$ -Iodopropane- $\beta\gamma$ -dicarboxylic Acid.*—The ethoxy-acid (2 g.) was boiled for 2 hours with "Zeisel" hydriodic acid, and the ethyl iodide formed allowed to escape. The resulting solution was extracted with ether, and the extract washed with thiosulphate solution, dried, and evaporated. The residue immediately solidified with evolution of heat, and after crystallisation from ethyl acetate-ligroin had m. p.  $138^{\circ}$  (Found: C, 23.9; H, 2.7. Calc.: C, 23.2; H, 2.7%). It was identified by direct comparison and a mixed m. p. determination with a specimen of  $\alpha$ -iodopropane- $\beta\gamma$ -dicarboxylic acid prepared for the purpose.

*$\alpha$ -Bromopropane- $\beta\gamma$ -dicarboxylic Acid.*—The ethoxy-acid was boiled for 3 hours with hydrobromic acid ( $d$  1.49), and the product extracted with ether. The residue obtained at once solidified, and after crystallisation from ethyl acetate-petrol had m. p.  $137^{\circ}$ . It was identified by the m. p. of a mixture with a genuine specimen.

*Paraconic Acid.*—Both the iodo- and the bromo-acid were treated with excess of silver oxide in aqueous suspension; heat was generated and the silver halide precipitated. The acid extracted with ether after addition of mineral acid solidified in an evacuated desiccator and then melted at  $50$ – $53^{\circ}$ . After crystallisation from ether-chloroform, paraconic acid was obtained, m. p.  $57^{\circ}$ , and identified by direct comparison and a mixed m. p. determination with an authentic specimen.

We take this opportunity to record our thanks to both the Chemical Society and the Royal Society for grants with the aid of which the cost of this investigation has been defrayed.

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## CXCIV.—*The Constitution of Polysaccharides. Part IX. The Degradation of Cellulose to an Anhydrotrisaccharide.*

By JAMES COLQUHOUN IRVINE and GEORGE JAMES ROBERTSON.

In former papers from this laboratory it was shown that cotton cellulose is composed of 1:5-anhydroglucose residues\* and the question was discussed as to the number of such residues present in the unpolymerised molecule of the polysaccharide. It was

\* See Appendix for discussion and revision of numerical nomenclature as applied throughout this paper.



pointed out (Irvine and Hirst, J., 1923, 123, 518) that the simplest view which satisfies the primary conditions is that cellulose is a polymerised di(1 : 5-anhydroglucose) (*loc. cit.*, p. 524, Formula IV) but that a formula of this type is at variance with the highest authentic yield of cellobiose octa-acetate so far obtained from a normal cellulose. In order to accommodate this result and yet preserve the greatest simplicity of structure, it was suggested that cellulose may be regarded as a polymeride of tri-1 : 5-anhydroglucose. The suggestion was tentative, as shown by the following significant extract from the argument:—"in the meantime it is prudent to select a formula for cellulose which will give a yield of cellobiose approximating to this figure (50—60%) rather than to the higher value 105.5." The same reasonable caution has been exercised in our other references to this question, but nevertheless the views expressed have been generally invested with a rigidity and finality for which no claim was made. The present position is that the exact number of anhydroglucose residues which form the cellulose molecule remains unknown and speculation regarding this factor must be guided from time to time as knowledge accumulates. Recently, X-ray spectrographic methods have been brought to bear on the problem and the results are interpreted as indicating that the  $C_6$  residues are marshalled in even numbers. This conclusion is opposed to the idea that the molecular unit is an anhydro-trisaccharide, but the results of standard chemical methods of attacking constitutional questions must equally be taken into account, even if, for the time being, they conflict with data obtained by purely physical processes. Obviously, the anhydro-trisaccharide formula need no longer be considered if convincing chemical evidence is forthcoming that the cellulose molecule is of a single type and definitely contains an even number of  $C_6$  residues. But it will be generally agreed that the acceptance of any particular molecular formula must rest ultimately on the depolymerisation of cellulose to the simplest non-reducing compound possessing the empirical formula  $C_6H_{10}O_5$  and retaining the 1 : 5-anhydro-linking. Further, such a compound should be capable of undergoing the reverse change of polymerisation without disturbance of the characteristic 1 : 5-anhydride ring and without forming complex glucosides of the type produced by the polymerisation of glucosan (Irvine and Oldham, J., 1925, 127, 2903). This prospect is still remote, but we now submit experimental evidence, bearing on the problem, which has been obtained by studying the graded acetolysis of cotton cellulose.

A review of the scattered literature and more particularly of papers which have appeared in the past few years reveals that acetolysis is an extremely complex process and is not confined to a

succession of reactions conducted on cellulose triacetate. Much recent work rightly emphasises the esterifying effect of the sulphuric acid employed in acetolysis, but nevertheless the earlier researches of Klein and of Schliemann reveal the essential nature of the changes involved. These workers showed that even when the yield of cellulose octa-acetate is as much as 60% of the cellulose used, degradation products persist which may be regarded as simple dextrans and possess a greater complexity than a disaccharide. These dextrin acetates are dextrorotatory and appear to be the immediate precursors of cellobiose octa-acetate, so that acetolysis may be regarded as a series of ill-defined steps as represented below. The scheme does not include the formation of aceto-sulphates as, from the point of view of the present investigation, these products arise from secondary reactions, and as cellulose has been completely converted into 2 : 3 : 6-trimethyl glucose, it is also unnecessary to make separate provision for isocellobiose acetate.

Cellulose  $\rightarrow$  Acetylated cellulose  $\rightarrow$  Acetylated cellulose dextrans  $\rightarrow$   
[X]  $\rightarrow$  Cellobiose octa-acetate  $\rightarrow$  Glucose penta-acetate.

Acetylation and depolymerisation are the essential features of the earlier reactions, and the opening of anhydro-rings by hydrolysis is specially characteristic of the two final stages, but there is no sharp line of demarkation between these different types of change. The hypothetical stage indexed as [X] therefore represents the formation of compounds in which the maximum depolymerisation of cellulose has taken place, whilst the specific hydrolytic action responsible for the formation of cellobiose octa-acetate is a minimum. The present investigation deals with the exploration of this group of acetolysis products.

Several workers, notably Bertrand, Hess, and Pringsheim, have occupied themselves with what is essentially the same subject of research and have obtained results of great interest. It is, however, a difficult matter to define exactly the experimental conditions under which acetolysis can be controlled so as to give consistent results. The physical condition of the cellulose used and the treatment to which it has been subjected, minute variations in the purity of the reagents employed, the temperature and other factors still unrecognised, combine to affect the series of reactions profoundly. In consequence, through no fault of the observers, the statements in the literature are occasionally conflicting. We find, however, that the progress of acetolysis can be ascertained by systematic physical examination of samples of the product and that it is possible to arrest the reactions at a stage immediately before cellobiose octa-acetate is formed and when insoluble dextrans are

present in minimum amount. This result was secured by working between two limiting conditions, the first being that no trace of crystalline structure should be observable in the solid product when examined by ordinary microscopic methods. Control experiments showed that as small a proportion as 3% of cellobiose octa-acetate can be identified with certainty in this way. The second limiting condition was that a solution of the product in chloroform should be dextrorotatory and should show only a faint cone of light when viewed in the ultramicroscope. This secured that insoluble dextrans constituted less than 7% of the total. The product obtained when these conditions were preserved was a white amorphous powder and the composition was that of a cellulose triacetate, but its properties presented a sharp contrast with those of a normal acetate of the polysaccharide. In particular, it displayed a much wider range of true solubility, possessed a distinct, although indefinite, melting point, and was dextrorotatory. The change of sign from the laevorotation characteristic of cellulose triacetate is in itself proof that extensive depolymerisation had taken place. Despite the uniformity in properties and composition displayed by different preparations, the product was a mixture and contained at least two constituents which reduced Fehling's solution, the ratio of the cuprous oxide formed before and after acid hydrolysis being 1 : 2.2. The greatest caution must be exercised in interpreting all analytical data in the case of acetolysis products and consequently the nature of the degraded acetate was ascertained by submitting it to (1) deacetylation and (2) methylation. Treatment with aqueous dimethylamine eliminated the acetyl groups and enabled dextrans to be removed. The main product thus obtained was freely soluble in water but, owing to secondary reactions between reducing groups and the alkaline reagent (Irvine, Thomson, and Garrett, J., 1913, 103, 238), the material was contaminated with alkylamino-derivatives and could not be completely separated into its constituents. This section of our work is being continued, but it may be stated that we have isolated from the above mixture an amorphous disaccharide which was present to the extent of about 20%. The sugar melted with decomposition at 180°, and had  $[\alpha]_D + 14^\circ$  in water, but until this extension of the research is complete it is impossible to characterise the compound definitely as an *isocellobiose*.

These experimental difficulties were overcome by submitting the mixture of degradation compounds to the methylation process, which was adjusted so as to eliminate both alkylated disaccharides and dextrans. Contrasted with the behaviour of cellulose under parallel conditions, the methylation proceeded with remarkable smoothness and no difficulty was experienced in obtaining the fully

substituted derivative, a result which supplies additional evidence that extensive depolymerisation of the polysaccharide had been accomplished. As only the material insoluble in sodium hydroxide was collected, any disaccharide or monosaccharide constituents were retained in the alkaline liquors and were thus eliminated. Methylated dextrans, amounting to 6% of the total weight, were left undissolved on treatment with ether, so that, so far as molecular complexity is concerned, the product finally isolated was intermediate between lower dextrans and disaccharides. In this way, a 50% yield of a white, amorphous powder was obtained which was readily soluble in organic solvents, and possessed the properties of a glucoside. Molecular-weight determinations by the cryoscopic method in benzene solution, and confirmed by Rast's process, gave the value 656, showing that the substance was derived from a trisaccharide. The analytical composition also corresponded exactly with that required for  $[C_6H_7O_2(OMe)_3]_3$  and the combined results might well have been accepted at this stage as conclusive. The behaviour on hydrolysis, however, warrants the conclusion that only 70% of the material consisted of tri(trimethyl anhydroglucose), the remainder being the corresponding methylated trisaccharide. This evidence was obtained by heating with acid methyl alcohol, which effected hydrolysis and the condensation of the liberated sugars with the solvent. The product of this reaction was isolated by vacuum distillation and consisted of a mixture of trimethyl methylglucoside (90%) with tetramethyl methylglucoside (10%). This opinion was verified in two ways. The mixture of glucosides was hydrolysed and the sugars thus obtained consisted exclusively of 2:3:6-trimethyl glucose and 2:3:5:6-tetramethyl glucose, both of which were isolated in crystalline form in yields which correspond with the above composition. Further, precisely the same result was obtained when the original methylated product was hydrolysed by means of aqueous acid to give the corresponding sugars directly without the intermediate formation of the glucosides. The combined evidence leads to the opinion that, under the conditions specified, cellulose can be degraded to a mixture of acetates derived from the following compounds in the proportions stated:—

1. Dextrans .....	6%	3. Triglucose .....	15%
2. Anhydro-triglucose .....	35%	4. Diglucose .....	20%

Although the results clearly favour the idea that anhydro-triglucose forms part of the cellulose aggregate, the possibility remains that anhydro-diglucose molecules may also be concerned in the polymerisation which leads to the polysaccharide. This possibility has been foreshadowed by the work of Irvine and Oldham (*loc. cit.*), who showed that the polymerisation of  $\beta$ -glucosan

involves both odd and even numbers of the monomeric unit, and is emphasised by consideration of the yields of the various products obtained in the present research. Although our work was carried out under conditions as nearly as possible quantitative, only 76% of the degraded acetates was accounted for in the form of pure derivatives. Further, during the original acetolysis, about 30% of the cellulose was converted into soluble or volatile products. Making allowance for these factors, it follows that the yield of trisaccharide derivatives actually obtained by us is of the order 35% when referred to the weight of cellulose originally employed. This is a minimum value and there seems no reason for doubt that at least one-third of the polysaccharide is based upon the triglucose unit. The remaining two-thirds of the polymerised aggregate remains unknown and the research is consequently being continued on the following lines: (1) the constitutional study of the tri- and di-saccharide products of graded acetolysis, (2) the polymerisation of these products and (3) the quantitative relationship between the tri- and di-saccharides.

#### *Discussion of Results.*

The views expressed in the present paper depend on the conversion of cellulose into simple methylated compounds, one of which is derived from triglucose and one from the corresponding anhydro-triglucose. Although it was possible to separate these two constituents from other compounds, it proved impossible to separate them from each other and thus the conclusions are in part based upon analytical figures. This in itself would be insufficient, but although there is ample supplementary evidence, it is necessary to discuss the results critically and to consider in how far explanations other than that offered are valid. Much depends on the fact that tetramethyl glucose is formed as a scission product when the above methylated mixture is hydrolysed, and the obvious suggestion is that the small amount of this sugar which was isolated may be traced to glucose penta-acetate or to cellobiose octa-acetate present in the original starting material. This possibility is discounted by the fact that the degraded acetates were amorphous, although this observation does not exclude the presence of an *isocellobiose* acetate. Of greater importance is the technique employed in the methylation which, on the basis of control experiments, was adjusted so as to eliminate both mono- and di-saccharides.

It is therefore evident that the tetramethyl glucose did not originate in glucose or in cellobiose, but in a polyhexose containing more than two  $C_6$  residues. If the methylated material which yielded the tetramethyl glucose consists of a single chemical individual,

it follows that ten  $C_6$  groups are present, but, in such an event, the molecular weight would exceed 2000. If, on the other hand, the material is a mixture, one component must be a fully methylated reducing sugar containing any number of glucose residues from three to nine, the remaining constituent being the corresponding poly(trimethyl anhydroglucose). The number of possible mixtures which satisfy the analytical data is large and in the following table some typical examples are given, all of which possess practically the same composition and would give the results obtained in this investigation.

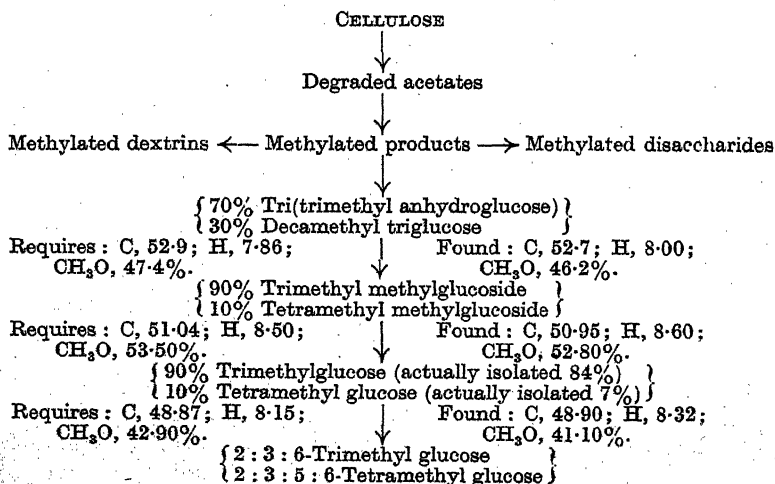
I. A mixture containing 70% of a tri(trimethyl anhydroglucose) and 30% of a methylated trisaccharide. (Molecular weight approximately 625.)

II. A mixture containing 60% of a tetra(trimethyl anhydroglucose) and 40% of a methylated tetrasaccharide. (Molecular weight approximately 834.)

III. A mixture containing 50% of a penta(trimethyl anhydroglucose) and 50% of a methylated pentasaccharide. (Molecular weight approximately 1043.)

IV. A mixture containing 40% of a hexa(trimethyl anhydroglucose) and 60% of a methylated hexasaccharide. (Molecular weight approximately 1251.)

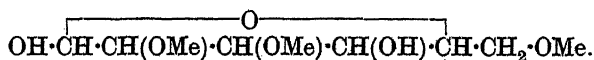
The list reveals that the molecular-weight determinations are discriminative and, as the value 656 was obtained, lead to a definite decision on the question of molecular magnitude. The consistency of our results is also displayed by the following scheme, which serves to simplify the series of reactions :



*Appendix.*

Subsequent to the completion of the paper now communicated, the subject of the ring structure of glucose has been re-opened by Charlton, Haworth, and Peat (this vol., p. 89), who bring forward evidence that the stable form of the sugar is an amylene-oxide. That the oxydic ring in glucose may occupy different positions was first experimentally verified by one of us ten years ago, and the necessity to take all the different possibilities into account has repeatedly been emphasised (Irvine, "Some Constitutional Problems in Carbohydrate Chemistry," *J.*, 1923, **123**, 900). For a considerable time it has been recognised by workers in this field that as the  $\gamma$ -oxydic formula for glucose depended on collateral rather than on direct experimental evidence, it might require modification and that to have the position of the oxygen ring settled experimentally would mark an advance in sugar chemistry. We do not commit ourselves at this stage to unqualified acceptance of the modified formula for glucose—the suggestion offered introduces a number of simplifications and is worthy of extended trial—but we defer our opinion until results obtained by the ultimate oxidation of tetramethyl glucose are available.

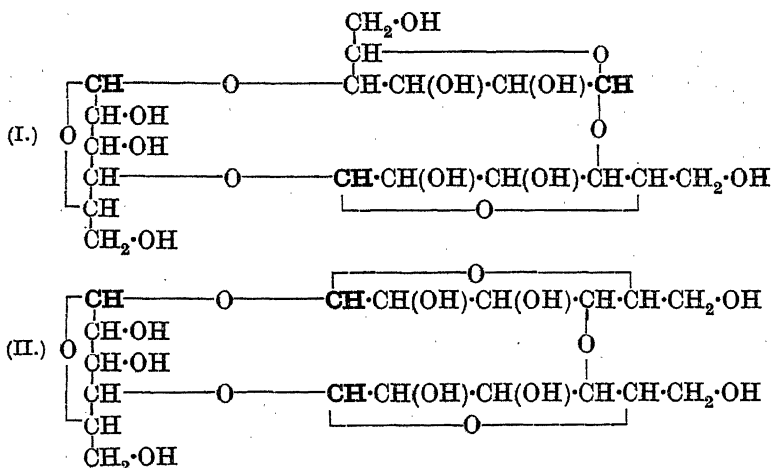
The formulæ of a number of methylated sugars may, however, be adjusted, *e.g.*, 2:3:5-trimethyl glucose would be described as the 2:3:4-form, but from the point of view of the present research greater importance is attached to the sugar known as 2:3:6-trimethyl glucose. A review of the constitutional study of this compound does not justify altering the position of the methyl groups, so that by shifting the ring to the neighbouring carbon atom the formula becomes :



The linkage present in cellulose would thus presumably be through positions 1 and 4 in place of 1 and 5 and the polysaccharide would therefore be described as poly-(1:4-anhydroglucose). It would, however, be premature to accept this conclusion as final, in view of the fact the particular variety of trimethyl glucose now under consideration can react as a  $\gamma$ -sugar. This possibility has been pointed out by Irvine and Hirst (*J.*, 1922, **121**, 1221) in their study of the condensation of the compound with methyl alcohol, and it follows that the formation of this sugar is not absolutely diagnostic as to the structure of the complex from which it originates. This possibility and its effect on constitutional questions are discussed in a forthcoming paper.

The application of a poly(1:4-anhydroglucose) structure to

cellulose may now be considered and the opportunity may be taken to simplify the alternative structural formulæ applicable to this unit, as further consideration has shown that, provided  $\alpha$ - and  $\beta$ -configuration is not taken into account, only two possibilities exist.\* These as modified are :



The position of the potential reducing groups is indicated in block type.

In view of the results communicated in this paper, and taking into account the increasing importance attached to the formation of *isocellobiose* from cellulose, it would be inadvisable to exclude formula II entirely. The retention of both types formulated above accounts for the formation of isomeric cellobioses and it is possible that both may function, although unequally, in the polymerisation process which leads to cellulose.

#### EXPERIMENTAL.

*Graded Acetolysis of Cotton Cellulose.*—The material employed was provided by Mr. William Rintoul of Messrs. Nobels, Ltd., and was identical with that used in our other investigations (see previous papers). Systematic experiments showed that when the temperature at which acetolysis is conducted is maintained uniformly at 15°, the best results were obtained when the reagent consisted of acetic anhydride and sulphuric acid in the ratio of 5.9 parts to 1 part

\* I am indebted to Dr. A. Geake of the Shirley Institute (British Cotton Industry Research Association), who first kindly directed my attention to this simplification.—J. C. I.



by weight. These conditions having been established, the remaining factor, *viz.*, the duration of the reaction, was determined, in the first instance approximately, by microscopic examination of samples of the product. When precipitated by water, dissolved in alcohol, reprecipitated and dried, the material showed a wide range of solubility in organic solvents including benzene. These solutions, which were dextrorotatory, did not give films on evaporation and no trace of crystalline matter was visible in the residue, although control experiments with artificial mixtures showed that 3% of cellobiose octa-acetate can be detected in this way. Further, when dissolved in chloroform, the solution was practically optically clear when viewed in the ultramicroscope, a faint cone of light being, however, visible owing to the persistence of a small proportion of higher dextrans. The control experiments were conducted throughout the entire series of products ranging from a normal cellulose triacetate to cellobiose octa-acetate. A typical preparation is now described, but as the reaction is affected by numerous factors, including the surface condition of the cotton, it is necessary to state that in order to obtain consistent results the acetolysis must be standardised by the physical examination indicated above.

The cellulose (40 g.), dried at 110°, was added gradually to a mixture of 400 c.c. of acetic anhydride and 40 c.c. of sulphuric acid, the pasty mass being kept at 15° and thoroughly stirred for 5 hours. The cellulose was noticeably affected in 90 minutes and dissolved within 24 hours, giving a faintly yellow liquid. During the subsequent 72 hours the colour changed to orange, but the solution remained clear and as at this stage the ultramicroscopic test was satisfactory the liquid was poured into 4 litres of water. The solid thus precipitated showed a tendency to coagulate to a plastic mass which was disintegrated by grinding under water to give a fine flaky powder. After filtration, the product was thoroughly washed with water and dried slowly at 30–40°/10 mm. Thereafter it was dissolved in hot rectified spirit and reprecipitated by the addition of water. Average yield of dry solid = 50 g., when the duration of the acetolysis varied from 95 to 101 hours.

The material was only slightly soluble in hot absolute alcohol, but easily soluble in rectified spirit. It was also readily soluble in cold acetic acid, acetone or chloroform, but less so in benzene. It melted without decomposition, but the temperature of fusion varied between 120° and 160° in different preparations. Moisture (determined at 110°), 1.35%; ash, negligible; sulphur, absent. Found: C, 49.9; H, 5.8; Acetyl, 64.2. Cellulose triacetate requires C, 50.0; H, 5.55; Acetyl, 62.5%. The specific rotation varied

from about  $+10^{\circ}$  to  $+20^{\circ}$ , but in the work now described material was selected which gave the following values :

Preparation	Solvent.	c.	$[\alpha]_D$ .
I.	Chloroform.	1.75	$+20.3^{\circ}$
II.	"	2.58	19.4
III.	Acetone.	1.76	22.1

The acetate reduced Fehling's solution and as this result is important experimental details are given. A weighed quantity (0.3289 g.) was dusted into an excess of boiling Fehling's solution, the boiling being continued for 4 minutes. The weight of dry cuprous oxide thus obtained was 0.1467 g. In order to determine the effect of hydrolysis on the reducing power, 0.3289 g. of the acetate was dissolved in 60% alcohol containing 6% of hydrogen chloride, and the solution was boiled under a condenser for 4 hours. Thereafter the alcohol was replaced by 8% aqueous hydrochloric acid, and the mixture again boiled for 8 hours. A trace of solid matter remained undissolved and the solution, which was practically colourless, was neutralised and added to boiling Fehling's solution. As the weight of cuprous oxide obtained was 0.3250 g., the ratio of the reducing power before and after hydrolysis is 1 : 2.2. Attempts to eliminate the reducing component of the mixture effected only negligible separation but revealed, as the following experiment shows, that little significance can be attached to melting points in these compounds.

18 G. of the acetate were dissolved in 250 c.c. of hot rectified spirit and, on cooling, a first fraction of 12 g. separated. On adding 270 c.c. of water to the mother-liquor a precipitate formed and after further dilution to 850 c.c. the liquid was set aside over-night. The second fraction thus obtained weighed 5.4 g.

	Original material.	Fraction I.	Fraction II.
M. p. ....	$155^{\circ}$	$130-140^{\circ}$	$140-148^{\circ}$
C .....	49.9%	49.6%	49.6%
H .....	5.8%	5.75%	5.6%
$[\alpha]_D$ in chloroform ...	$+18.5^{\circ}$	$+20.3^{\circ}$	$+19.4^{\circ}$

Molecular weight determinations by Rast's process or by the cryoscopic method in acetic acid gave very variable results, owing apparently to the presence of a small quantity of insoluble dextrin. The presence of this impurity was confirmed by digesting the acetate with 2*N*-sodium hydroxide at  $25^{\circ}$  for 3 hours. On neutralisation, a flocculent precipitate separated which darkened on washing and drying. This product, which was present only in small amount, had the properties of a dextrin, decomposed at  $220^{\circ}$ , and gave C, 44.5; H, 6.4% [ $(C_6H_{10}O_5)_x$  requires C, 44.4; H, 6.2%].

*Methylation of the Depolymerised Acetate.*—As the direct replace-

ment of acetyl by methoxyl in one operation is not of general application, the details of a typical experiment are quoted. The acetate (46 g.) was suspended in 225 c.c. of 2*N*-sodium hydroxide and disintegrated by mechanical stirring. After the temperature had been raised to 30°, small equivalent quantities of methyl sulphate and 30% sodium hydroxide were added at short intervals and, when three-fourths of the reagents had been introduced, the temperature was gradually raised to 70° and maintained at this point until the remainder of the methylating mixture had been added. Total reagents used : 110 c.c. of methyl sulphate and 110 g. of sodium hydroxide in 180 c.c. of water.

After completion of the reaction by heating at 100° for 35 minutes, the product remained in solution and was extracted with chloroform. The extract was dried and the solvent removed, when a clear syrup remained which set on cooling to a glass. Yield, 14 g.; OMe, 38.1%. The products of three similar preparations were united and subjected to three further methylations. As the methoxyl content increased, the solubility in alkali diminished so that the methylated product could be removed by filtration and, an important point, the process of chloroform extraction was discontinued so that the disaccharide derivatives remained in the alkaline liquor. Yield, 30 g.; OMe, 45.6%. Five subsequent methylations did not affect the methoxyl content, which agrees exactly with that required for a trimethyl cellulose.

The product was ground to a white solid and extracted repeatedly with boiling ether, which left a small residue (6%) undissolved. This had OMe, 43.7%, and was evidently derived from the cellulose dextrin present in the starting material. On removal of the solvent ether, the main product (94%) was isolated as a clear, colourless glass which could be powdered to a fine white solid softening at about 40°. This proved to be essentially tri(trimethyl 1 : 5-anhydroglucose) mixed with the corresponding methylated trisaccharide. Properties : readily soluble in cold ether, chloroform, benzene, or acetone, less soluble in methyl alcohol, rectified spirit or water ; no action on Fehling's solution until after acid hydrolysis. Found : C, 52.7; H, 8.0; OMe, 46.2. A mixture of 70% of tri(trimethyl anhydroglucose) and 30% of a fully methylated trisaccharide requires C, 52.9; H, 7.9; OMe, 47.4%.

Solvent.	c.	$[\alpha]_D^{20}$ .
Chloroform .....	3.564	+7.0°
Benzene .....	1.682	10.1
Acetone .....	3.367	15.7

*Molecular Weight.*—The mean of two determinations by Rast's method was 662. The mean of three consistent results by the

cryoscopic method with benzene as solvent was 663, and an independent repetition of the same process gave 642. The calculated value for the mixture postulated above is 625.

*Simultaneous Hydrolysis and Condensation with Methyl Alcohol.*—The mixture of methylated trisaccharide derivatives (4.3552 g.) was dissolved in methyl alcohol containing 1% of hydrogen chloride and heated at 110° for 70 hours. The solution, which was pale yellow and contained no suspended matter, was then neutralised with silver carbonate, filtered, and evaporated to dryness. 4.562 G. of a colourless glucosidic syrup remained, corresponding with a yield of 92% of the theoretical maximum. On distillation, the liquid boiled at 115°/0.3 mm. and 3.87 g. were collected in two fractions to permit of duplicate analyses. On the basis that the original methylated is a mixture of 70% of tri(trimethyl anhydroglucose) and 30% of a fully methylated trisaccharide, the above product of hydrolysis should consist of trimethyl methylglucoside (90%) and tetramethyl methylglucoside (10%). This was verified by analysis. Fraction I: C, 50.9; H, 8.3; OMe, 52.6. Fraction II: C, 50.95; H, 8.6; OMe, 52.8%. Calculated for the mixed glucosides: C, 51.0; H, 8.5; OMe, 53.5%.

*Hydrolysis of the Mixed Glucosides.*—The syrup (2.67 g.) was dissolved in 110 c.c. of 8% hydrochloric acid, a trace of charcoal added, and the solution boiled under a condenser until the rotation was constant. The subsequent treatment was as usual and as the mixed sugars, isolated initially as a syrup, weighed 2.2 g., the yield was 88%. In order to separate the sugars, the syrup was dissolved in water, and the solution thoroughly extracted with chloroform. The aqueous solution was evaporated to dryness under diminished pressure, the resulting syrup being redissolved in absolute alcohol which was, in turn, evaporated. Finally, the sugar was dissolved in pure dry ether and after filtration the solvent was slowly evaporated. On nucleation with 2:3:6-trimethyl glucose, the product solidified to a hard mass of crystals (1.85 g.), m. p. 105°; permanent  $[\alpha]_D$  in water, for  $c = 1.058$ , + 71.8° (Found: C, 48.5; H, 8.05; OMe, 41.6. Calc.: C, 48.65; H, 8.1; OMe, 41.9%).

The remaining methylated sugar was isolated from the chloroform solution, which was dried and evaporated, as a syrup weighing 0.25 g. This crystallised on keeping and, when purified from light petroleum, gave pure 2:3:5:6-tetramethyl glucose displaying the standard physical constants. Yield of trimethyl glucose: yield of tetramethyl glucose = 84%:7%. Calc., 90%:10%.

*Direct Hydrolysis of the Methylated Product.*—A 5% solution in 8% hydrochloric acid was fully hydrolysed on boiling for 30 minutes, and the sugars formed were isolated by standard methods. The

product was a clear syrup which, in accordance with the composition of the starting material, should consist of trimethyl glucose (90%) and tetramethyl glucose (10%) (Found: C, 48.9; H, 8.3; OMe, 41.1. The above mixture requires C, 48.9; H, 8.15; OMe, 42.9%).

*Deacetylation of the Degraded Cellulose Acetates.*—20 G. of the finely-powdered acetate were added to 66 c.c. of 33% aqueous dimethylamine. An appreciable rise of temperature took place and the liquid was cooled to 15° and kept, with frequent shaking, for several days. For the first 48 hours the liquid thickened, but after 96 hours it had become much more mobile. After 9 days, water was added and insoluble dextrans were removed by filtration through charcoal, the filtrate being evaporated to dryness under diminished pressure. A golden syrup remained which was thoroughly mixed with successive quantities of ether to remove acetodimethylamide, the undissolved residue being dissolved in a little water and precipitated by excess of absolute alcohol. A white, amorphous powder was thus obtained (1.85 g.) which sintered at 170° and melted with decomposition at 180° (Found in material dried in a vacuum at 110° until of constant weight: C, 42.3; H, 6.6; *M*, cryoscopic in water, 315. A disaccharide requires C, 42.1; H, 6.4%; *M*, 342). The product is therefore a disaccharide other than cellobiose; it reduced Fehling's solution both before and more particularly after hydrolysis with acids. For  $c = 4.2735$ ,  $[\alpha]_D^{20}$  was  $+14.04^\circ$ , no mutarotation being observed within 24 hours.

The alcohol mother-liquor which had yielded the above disaccharide gave on evaporation under reduced pressure 6.4 g. of a syrup. This was dissolved in water, the solution agitated with chloroform to remove traces of acetodimethylamide, and the aqueous portion neutralised and recovered. By means of fractional extraction with boiling alcohol, the material was separated into two portions, but it was found impossible to eliminate dimethylamino-glucosides, and consequently this section of the investigation is being continued by different methods.

Acknowledgment is made to the Carnegie Trust for the award of a Fellowship which enabled one of us to take part in the investigation.

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[Received, February 17th, 1926.]

CXCV.—*The Constitution of Polysaccharides. Part X.  
The Molecular Unit of Starch.*

By JAMES COLQUHOUN IRVINE and JOHN MACDONALD.

WE have naturally included the important case of starch as part of our programme of research on the constitution of polysaccharides, applying the same principles and methods as in the analogous examples of cellulose and inulin. The same limitations have also been imposed on the scope of the investigation, which has been confined meanwhile to determining the linkage of the individual glucose residues in starch so as to arrive at the structure of the simplest molecule (or molecules) which, by polymerisation, form the polysaccharide. Our work has not been concerned with the magnitude of these polymerides or with the individual constituents of starch, nor has it included the differences between one variety of starch and another so far as these may be attributed to variations in the nature and amount of extraneous compounds rather than to inherent differences in molecular structure.

Hitherto, the experimental evidence applicable to the constitutional study of starch has been obtained mainly through biochemical agency and, in introduction to the present communication, only two types of such reactions may be selected from the abundant literature on this subject. These are: (a) the conversion of starch into a series of simple amyloses in each of which the empirical formula  $(C_6H_{10}O_5)_n$  is retained, and (b) the formation, through changes which are in part hydrolytic, of maltose, isomaltose, and, ultimately, of glucose. An adequate structural representation of starch must accommodate the above reactions and it is evident that the constitution of maltose is of special importance as bridging the gap between the closed-ring structure of the polyamyloses and the  $C_6$ -chain of glucose. Generally speaking, the application of ordinary chemical methods has led to few results which bear directly on the constitution of starch, as the processes of substitution and disruption are not sharply differentiated. An exception is provided, however, in the method of methylation, by means of which the hydroxyl groups in starch may be substituted by methoxyl groups which survive hydrolysis, thereby giving a methylated glucose. Work on these lines was commenced in this laboratory 6 years ago, but no detailed account of our results has so far been published, although reference has been made occasionally to some of the conclusions at which we have arrived. The delay has been due, not so much to the fact that the methylation of starch presented severe

experimental difficulties, as to the necessity which arose to suspend the research and devote a series of separate investigations to the constitution of maltose. Meanwhile, other workers have attempted to convert starch into its fully methylated derivative, but have failed, it having been found impossible to replace all the hydroxyl groups by methoxyl. Our experience in this respect was, at first, no different, and consequently we were compelled to subject an incompletely methylated starch to hydrolysis and to separate the mixture of methylated glucoses thus produced. In such constitutional studies, this is unsatisfactory procedure and cannot be regarded as giving an adequate view of structure, but our earlier work revealed that an invariable product of the reaction was a crystalline sugar, which was identified as 2 : 3 : 6-trimethyl glucose. This result was altogether unexpected. Unless the action of diastase on starch is in part synthetic, there can be little reason to doubt that, in the starch molecule, glucose residues are joined in the same manner as in maltose, and it follows that the trimethyl glucose obtainable from starch should be identical with that from maltose. Haworth and Leitch, however, state that the disaccharide gives 2 : 3 : 4-trimethyl glucose, and the formula for maltose advocated by these authors, either in its original form (J., 1919, 115, 809) or as subsequently modified (Charlton, Haworth, and Peat, this vol., p. 99), does not admit of the formation of 2 : 3 : 6-trimethyl glucose from any compound containing the maltose structure. The evidence before us was thus conflicting. Obvious sources of error, such as the possible presence of hemi-celluloses, had been carefully excluded, but other explanations suggested themselves, one being that the glucose residues in starch might not be symmetrically attached to each other, as one pair might possess the maltose structure and another the linkage characteristic of cellobiose. This idea was expressed in formulæ (*Brit. Assoc. Reports*, 1922, 33; J., 1923, 123, 898) in which an attempt was made to reconcile our results with those from which the structure of maltose was deduced, but further investigation showed that no satisfactory formula for starch could be constructed on the basis of Haworth's constitution of maltose. This became apparent when we succeeded in methylating starch completely, as, on hydrolysing the product, 2 : 3 : 6-trimethyl glucose was obtained in yields which showed that this sugar must be regarded as the essential and not as an adventitious product of the series of reactions. Concurrently, and by arrangement with Professor Pringsheim, hexa-amylose was subjected similarly to methylation and hydrolysis. The result was equally emphatic, as the same crystalline sugar was obtained as from starch. Finally,

the tri-hexosan prepared by the depolymerisation of starch (Pictet, *Helv. Chim. Acta*, 1922, 5, 640; 1924, 7, 932) was similarly treated and was likewise found to give the same variety of trimethyl glucose.

Only two alternative conclusions could be drawn from the above discordant evidence; the first, that maltose has no structural relationship to starch, was rejected as improbable and we were forced to the opinion that the constitution attributed to maltose was incorrect. This we have ascertained to be the case (Irvine and Black, this vol. p. 862), it having been shown that, in common with starch, polyamyloses and cellulose, maltose yields 2 : 3 : 6-trimethyl glucose unmixed with the 2 : 3 : 4-isomeride. The present communication is therefore submitted on the basis of a corrected constitution for maltose.

We find that the methylation of starch displays a number of features which distinguish the polysaccharide from either cellulose or inulin. Methyl groups are introduced fairly readily by repeated action of methyl sulphate and alkali, but the methoxyl content quickly reaches a limit of 36—37%, this value indicating that only seven hydroxyl groups out of nine have undergone alkylation. Methylated starch of this composition appears to be a definite compound possessing a characteristic optical activity, and, in consequence, the conclusion might be drawn that there are not three hydroxyl groups in each  $C_6$  unit. This inference would be unwarranted, however, as the partly methylated starch was capable of acetylation to the exact extent required to substitute the remaining hydroxyl positions. Further, the methylated starch, when regenerated from the acetate, still preserved its resistance to further methylation. Another distinguishing property displayed by starch during methylation is that the reaction is definitely arrested at the dimethyl stage when conducted by means of silver oxide and methyl iodide. When these reagents are applied to a methylated starch containing less than two methoxyl groups per  $C_6$  unit, the methoxyl content is increased to 32—33%, but no further. Similarly, the same reagents have only a limited effect in raising the methoxyl content when applied to methylated starch which has been alkylated by means of methyl sulphate beyond the dimethyl stage. In the above respects, starch resembles the polyamyloses closely and presents features which are also recognisable in the case of maltose. As the methylation of starch proceeded, the colour reaction with iodine vanished, the usual progressive changes in solubility were observed, and the rotation increased in the dextro-sense. Simultaneously, the protein and inorganic constituents were eliminated, particularly when the



silver oxide reaction was employed, as, in this case, they were precipitated in the form of insoluble double compounds with silver iodide. It is important to observe that these precipitates contained combined carbohydrate, thus indicating that nitrogen and phosphorus form part of the polymerised aggregate. In consequence, the same methylated starch was finally obtained, irrespective of the starting material used, but in large-scale experiments we employed only purified rice-starch. Reference to the experimental details will indicate the manner in which the derivatives of hemi-celluloses were removed so as to separate constituents which would otherwise have introduced complications.

Although four successive applications of methyl sulphate and alkali converted the polysaccharide into a derivative containing 37% of methoxyl, this did not represent the limit of the reaction. Subsequent methylations slowly increased the methoxyl content and, after 24 treatments, the value (43.7%) agreed closely with that required for a trimethyl starch. There are thus three distinct stages observable in the alkylation, the products in each case displaying a constancy in composition and properties which warrants the conclusion that they are three consecutive compounds. These are :

	% OMe (found).	Ratio of OMe groups to initial OH groups.	$[\alpha]_D$ in $\text{CHCl}_3$ .
I. Dimethyl starch .....	32.7	6 : 9	+ 135.7°
II. Methylated starch .....	36.3	7 : 9	169.5
III. Trimethyl starch .....	43.7	9 : 9	216.5

It will be observed that the specific rotation increased regularly with the rise in methoxyl content, and this behaviour we have verified over a wide range in composition, thus affording powerful evidence that frequent repetition of the methylation process does not cause structural rearrangement.

The hydrolysis of each type of methylated starch was undertaken, the method of heating with methyl alcohol and hydrogen chloride being employed so as to isolate the liberated sugars in the form of the corresponding methylglucosides. Compound I gave essentially a dimethyl methylglucoside, the description of which is deferred to a later communication, while II yielded a mixture from which 2 : 3 : 6-trimethyl methylglucoside (1 mol.) was isolated, together with a dimethyl methylglucoside (2 mols.). In the case of III (trimethyl starch) the reaction furnished a conclusive result, as 2 : 3 : 6-trimethyl methylglucoside melting at 57.5° was obtained in excellent yield. A careful search for the isomeric 2 : 3 : 4-form was made, both by fractional distillation and by fractional crystal-

lisation of the glucoside, but no trace of this compound was detected. These results were confirmed by hydrolysis of the total glucosides with aqueous acid and isolation of crystalline 2 : 3 : 6-trimethyl glucose. All syrupy products were examined, but the 2 : 3 : 4-isomeride was definitely absent.

In the course of this section of our work it was necessary to compare critically the constants of the isomeric 2 : 3 : 6- and 2 : 3 : 4-trimethyl  $\beta$ -methylglucosides, as these compounds, which show a close resemblance, have been utilised in certain structural studies of disaccharides as a means of discriminating between the isomeric trimethyl glucoses. The following values were determined on specimens of the compounds obtained either by the limited action of methyl alcohol and hydrogen chloride or through the agency of the corresponding acetobromo-derivatives.

	Source.	M. p.	$[\alpha]_D$ .
2 : 3 : 6-Trimethyl methyl-glucoside.	2 : 3 : 6-Trimethyl glucose from cellulose, or Trimethyl starch.	57.5°	-29.3° in MeOH
2 : 3 : 4-Trimethyl methyl-glucoside.	2 : 3 : 4-Trimethyl glucose (synthetic), or Trimethyl glucosan.	93—94	-23.1 in MeOH

The glucosides cannot be distinguished with certainty through their specific rotations, and the melting points, although far apart, are greatly affected by impurities or by the presence of varying proportions of  $\alpha$ - and  $\beta$ -forms. It follows that trustworthy identification of these reference compounds is possible only when both the melting point and the specific rotation agree with the standard values. In addition, the polarimetric curve of the hydrolysis of each compound is diagnostic, and in the case of the equilibrium mixture of the  $\alpha$ - and  $\beta$ -2 : 3 : 6-isomerides displays two maxima separated by a minimum. The identification of these isomeric glucosides is nevertheless difficult and failure to discriminate between them may lead to erroneous conclusions as to structure. In this connexion, it may be recalled that Haworth and Wylam (J., 1923, 123, 3125) obtained from gentiobiose a trimethyl methylglucoside melting at 92.5° and showing  $[\alpha]_D$  -25.1° in methyl alcohol. This was regarded as the 2 : 3 : 4-variety, a conclusion which is doubtless correct. But in studying the constitution of raffinose (Haworth, Hirst, and Ruell, J., 1923, 123, 3131) another preparation, possessing nearly the same specific rotation, but melting at 74°, is also claimed to be 2 : 3 : 4-trimethyl methylglucoside. The statements are irreconcilable, as, if the melting point of the latter preparation was depressed by the presence of the stereoisomeric  $\alpha$ -form, the specific rotation would

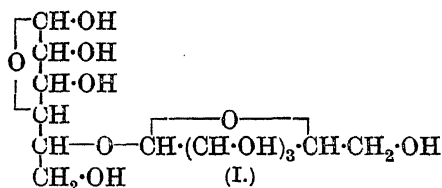
not remain the same, but would be displaced in the dextro-direction. In our examination of these glucosides we have never encountered a form of 2 : 3 : 4-trimethyl methylglucoside melting at 74° and the inconsistency becomes more acute if it be assumed that this figure is a misprint for 94°. We cannot accept, therefore, Haworth's constitution for raffinose, a conclusion further justified by the fact that it contains a melibiose residue based on the formula for maltose recently shown to be incorrect.

### *Discussion of Results.*

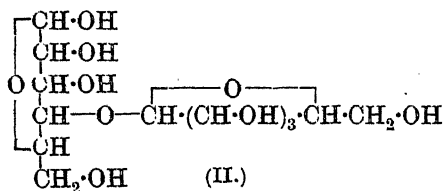
As starch is not a uniform homogeneous polysaccharide, limitations must be placed on any discussion regarding constitution, but the results now contributed afford proof that starch consists essentially of a mixture of polymerides which are based on the same molecular unit. The structural similarity displayed by these constituents lies in the fact that there are three hydroxyl groups present in the same positions in each  $C_6$  chain, and it is thus possible to elucidate the constitutional factors which are common to all the components. The expression "starch," as used in this discussion, applies therefore to constituents, amounting to 60—70% of the total, which conform to the above generalisation in that they are convertible into 2 : 3 : 6-trimethyl glucose, but differ in the degree of polymerisation.

The possibility that starch may be derived from  $\beta$ -glucosan has already been rejected and is again refuted by the results of the present investigation. There remains consideration of the relationship to maltose and to isomaltose, but here complications are at once encountered. These difficulties are due in part to inadequate knowledge of isomaltose, but are mainly attributable to the confusion which has arisen regarding the constitution of the diglucoses as a class. So far, three disaccharides (maltose, cellobiose, and isocellobiose) have been shown to be convertible into 2 : 3 : 6-trimethyl glucose, and the present research clearly points to the idea that isomaltose will be found to give precisely the same result. The formation of the above trimethyl glucose cannot, in consequence, be regarded as final evidence of the linkage of two glucose residues, as such a result fails to discriminate between two alternatives. It follows, also, that the oxydic ring in glucose cannot be restricted to the amylenoxide linkage alone, as otherwise it would be impossible to formulate all the diglucoses in terms of their properties. For example, the disaccharides postulated below are definitely isomeric and contain glucose residues with different oxygen rings, but each compound would be convertible into 2 : 3 : 6-trimethyl glucose, type I giving in the first place the  $\gamma$ -form of the sugar which

reverts to the stable variety, while type II would give the same final product directly.



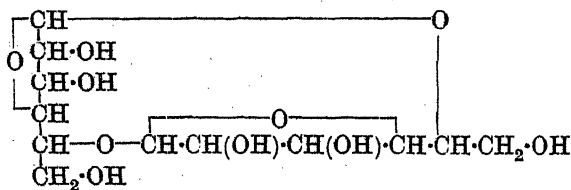
Glucose 5-glucoside.



Glucose 4-glucoside.

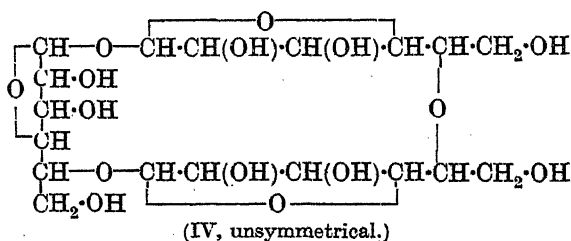
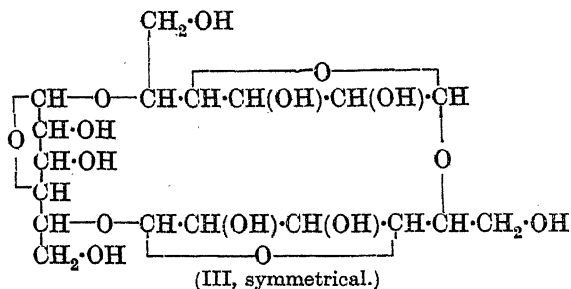
It may be presumed that as cellobiose and *isocellobiose* form one structural pair, maltose and *isomaltose* will form the other, and the above types can therefore accommodate all four sugars. Pending the completion of further experimental work now in progress, it is inadvisable definitely to assign maltose and cellobiose to their respective types, but, in order to render the present discussion intelligible, formula I may be ascribed arbitrarily to maltose, in which case cellobiose conforms to formula II.

If starch is based on an anhydro-disaccharide unit, the simplest formula for the unpolymerised molecule becomes :



The hydrolysis of the "maltosan" postulated above would give maltose as the only disaccharide, the change including opening of one anhydro-linking followed by adjustment of the unstable oxygen ring in the non-reducing glucose component. Taking into account the difficulty in certifying that any preparation of maltose consists of a single homogeneous chemical individual, it is doubtful if the yield of maltose from starch is as great as that which would be given by a compound of the maltosan type. It would not be justifiable, however, at this stage to exclude maltosan as one of the molecular

units of starch, particularly as polyamyloses exist which contain an even number of  $C_6$  chains. The formula does not, however, admit of the formation, from starch, of a trihexosan or tri-amylose, and consequently consideration must also be given to a constitution based on the union of three glucose residues. Two possibilities exist :



No conclusive evidence exists which would serve to discriminate between these possibilities. A compound possessing formula (III) could undergo hydrolysis to give only maltose and glucose, whilst, according to formula (IV), maltose, an isomaltose and a non-reducing diglucose might result. This is perhaps improbable, as the existence of such hydrolysis products could scarcely have escaped detection, but, in any case, neither of the formulæ reveals the  $\alpha$ - or  $\beta$ -configuration of the individual glucose residues. The structures thus fail to account for the fact that starch is convertible into maltose under one set of conditions and into isomaltose when the conditions are changed. Similarly, they do not explain why the polyamyloses can be classified in  $\alpha$ - and  $\beta$ -series.

We do not share the view that the  $\alpha$ - or  $\beta$ -configurations of the methylated glucosides obtained from trimethyl starch afford a true index of the glucose configuration in the starch molecule and purely chemical methods of investigation throw little light on this important aspect of the structural problem. This evidence is, however, rapidly being accumulated in the important researches of Ling and Nanji, and if the results obtained by these workers are not utilised in the

present discussion it is owing solely to the desire to avoid trespass on their field of work.

Limiting the discussion to conclusions drawn from chemical reactions alone, the structures elucidated above may now be tested according to the peculiar behaviour of starch during methylation. The formation of a definite dimethyl starch (*i.e.*, 6 hydroxyl groups out of 9 substituted) is explained in terms of either formula, as the primary alcohol groups are the last to be methylated. Both formulæ also accommodate the production of a trimethyl starch but only formula (IV) offers any explanation as to why methylation can be arrested at the dimethyl stage (*i.e.*, when 6 hydroxyl groups out of 9 have been substituted) and thereafter slows down abruptly when 7 hydroxyl groups out of 9 have been alkylated. For this reason, formula (IV) is retained for further consideration. Much importance must be attached to the fact that methylated starch containing 37% of methoxyl is a definite compound which breaks down on hydrolysis to give exactly 2 molecules of dimethyl glucose and 1 molecule of trimethyl glucose. Reference to the experimental part will show that this compound was obtained under varying experimental conditions on eight successive occasions, so that the composition ascribed to it is unlikely to be fortuitous. Accepting this result, it follows that the molecular unit of starch must contain either nine or a multiple of nine hydroxyl groups. In other words, the simplest unit would be a trihexosan and the next possibility a hexahexosan. In order to explain the existence of polyamyloses containing an even number of  $C_6$  chains, it is, however, necessary to select the hexahexosan as the basal unit, so that the cyclic formulæ given above must be doubled, with a corresponding increase in the structural possibilities involved.

It is thus apparent that, approaching the study of starch by strictly chemical methods, conclusions are reached in close agreement with those arrived at in recent studies of enzyme action. It will be equally apparent that both types of investigation are necessary to solve the main factors involved in the starch problem, (1) the  $\alpha$ - or  $\beta$ -configuration of adjacent hexose residues, (2) the positions through which these residues are coupled, and (3) the degree of polymerisation undergone by the basal unit.

The research, which we regard only as preliminary, is being continued in various directions.

#### EXPERIMENTAL.

The starting material used in the research consisted of purified wheaten, potato, or rice starch, but the first-mentioned variety was discarded in favour of the others, which were found to give the same

methyated derivatives. To facilitate description, it may be stated that, throughout the work, all evaporations and distillations were conducted under reduced pressure.

*Dimethyl Starch.*—With a few modifications, the methylation was carried out as described by Irvine and Steele (J., 1920, 117, 1474) in the parallel case of inulin, and the following is the account of one typical experiment. 32 G. of starch were mixed with 150 c.c. of water and stirred mechanically whilst 160 c.c. of 12½% sodium hydroxide solution were added. This had to be conducted slowly, as otherwise the starch coagulated to a stiff jelly, a condition which is unsuitable for methylation. Thereafter, 140 c.c. of 50% sodium hydroxide solution and 80 c.c. of methyl sulphate were run in simultaneously, the addition being extended over 3 hours and adjusted so as to maintain the alkaline reaction. The liquid was kept at 35° and was vigorously stirred during the reaction, which was completed by heating at 100° for 40 minutes. After cooling, an equal volume of rectified spirit was added, and carbon dioxide passed through the solution for a prolonged period. The precipitated sodium salts were then removed by filtration through linen, and the filtrate was cautiously neutralised with dilute sulphuric acid. If kept over-night, a crop of sodium sulphate and sodium methyl sulphate separated, but as part of the product was retained by the crystals it was advisable to evaporate the liquid to a thick syrup and repeat the methylation a second time on the total product. In this and similar evaporations it was necessary to add barium carbonate, as otherwise acidity developed and hydrolysis occurred. For the same reason, the temperature was restricted to under 60°.

The aqueous-alcoholic solution of the product, obtained after the second methylation, was evaporated to dryness, and the residue extracted repeatedly with a large excess of boiling chloroform. The inorganic residues were similarly treated and yielded a further quantity of the methylated product showing the same composition (OMe, 22.7—23.6%). A third methylation was conducted on the material extracted by chloroform and thereafter the methylated starch was completely soluble in aqueous alcohol and was no longer occluded by the inorganic salts. The isolation of the product by extraction with chloroform was carried out as already described, but difficulty was experienced in filtering the chloroform solution by ordinary methods, as the methylated starch formed continuous films on the filter-paper. On removal of the solvent, a stiff syrup remained, readily convertible into a white powder; soluble in cold water, hot alcohol, and in chloroform, insoluble in ether. Traces of reducing sugars were present and the aqueous solution gave a

yellow colour with iodine which was not discharged on heating. OMe = 27.2%. Yield 22 g.

The silver oxide reaction was now applied to the product, which was boiled with excess of methyl iodide to which methyl alcohol was gradually added until the solution became comparatively clear. Silver oxide (51 g.) was then added in small amounts, and the mixture kept at the boiling point for 8 hours. Boiling ethyl alcohol was used as the extracting agent, the turbid solution being evaporated and the residue dissolved in chloroform. The silver salts were also extracted in a Soxhlet apparatus with the same solvent, the extracts being united and the product recovered. Repetition of the alkylation in the same manner had very little effect on the methoxyl content, but, apparently owing to depolymerisation, the solubility of the product in methyl iodide increased steadily with each treatment. Concurrently, and contrary to general experience, the experimental loss increased with the solubility in methyl iodide.

No. of silver oxide methylations.	Wt. of methylated starch.	Vol. of MeOH required.	Methoxyl content.
1	21 g.	65 c.c.	27.8%
2	19	39	28.8
3	15	20	28.6
7	6	3	28.9

The loss in yield was due to combination of part of the product with silver iodide as in the case of methylating glucosamine (Irvine and Hynd, J., 1912, 101, 1128). On extracting the plastic solid with boiling water for several hours the solution contained carbohydrate, a secondary amine and phosphate.

Various attempts to purify the methylated starch obtained by the above operations were made, the most successful being boiling in chloroform solution with charcoal, but as this involved loss the material was separated into two portions by allowing an ethyl alcohol solution to stand in the cold. Any insoluble syrup which separated was removed and again methylated by the silver oxide reaction, so that ultimately the entire product was obtained in the soluble form. As the material had now acquired complete solubility in methyl iodide, two further methylations were given without the use of any extraneous solvent. In this way, dimethyl starch was obtained as a white powder, free from mineral matter and soluble in water, the solution giving no colour with iodine (Found: C, 50.4; H, 7.4; OMe, 32.7. Dimethyl starch requires C, 50.5; H, 7.4; OMe, 32.7%).  $[\alpha]_D$  in chloroform + 135.7° for  $c = 1.916$ .

*Hydrolysis of Dimethyl Starch.*—This reaction was conducted in the first place by heating a dilute solution in 2.5% hydrochloric acid on a boiling water-bath for 3 hours. As the solution remained turbid,



the acid concentration was raised to 4% and heating was continued for an additional 3 hours, the reaction being completed by raising the temperature to 110° for 30 minutes. On filtering, a small quantity of a brown solid remained behind, and as this material still contained methoxyl it apparently consisted of one component of dimethyl starch which is highly resistant to hydrolysis. The clear filtrate, containing dimethyl glucose in solution, was treated so as to remove organic acids and was finally extracted with boiling acetone. The extract contained a thick syrup which when dissolved in ethyl acetate partially crystallised, but the solid could not be isolated in sufficient amount for identification. The solubilities, rotation and analytical composition of the syrup were, however, identical with those ascribed to 2 : 3-dimethyl glucose (Irvine and Scott, J., 1913, 103, 575). Yield 75%.  $[\alpha]_D + 50.3^\circ$  in acetone for  $c = 1$  (compare 2 : 3-dimethyl glucose,  $[\alpha]_D + 50.9^\circ$  in the same solvent).

*Preparation of Methylated Starch.*

The expression "methylated starch" is applied to the derivative in which seven hydroxyl groups out of nine have undergone methylation, the formation of this compound being characterised by a sharp cessation in the methoxyl increase. In each experiment, 32 g. of starch were used, the initial procedure being as described in the preparation of the dimethyl derivative. After four successive treatments with methyl sulphate, the insolubility of the product in the alkaline liquor enabled the isolation to be greatly simplified. The liquid was poured away from the coagulated mass of organic material and the latter was dissolved in boiling rectified spirit, the solution being neutralised with dilute sulphuric acid. After removal of the precipitated sodium salts, the filtrate was evaporated in the presence of barium carbonate, and the residue extracted with boiling chloroform. Removal of the solvent left a stiff syrup which was boiled with dry ether to remove traces of solvent, a treatment which converted the product into a white flaky powder (Found in material dried at 100°/15 mm.: C, 51.1; H, 7.6; OMe, 35.5. "Methylated starch" requires C, 51.2; H, 7.5; OMe, 37.0%). Yield 21 g.

When the above methoxyl content had been attained the application of the silver oxide reaction had practically no effect on the composition (Found: C, 51.1; H, 7.5; OMe, 36.3%;  $[\alpha]_D$  in methyl alcohol  $+ 186.3^\circ$  for  $c = 1.934$ , in chloroform  $+ 168.1^\circ$  for  $c = 2.029$ ). Methylated starch displayed the same range of solubility as dimethyl starch and similarly had no action upon Fehling's solution. When acetylated by means of acetic anhydride in presence of sodium acetate, it was converted into a granular acetate showing  $[\alpha]_D$  in chloroform  $+ 191.7^\circ$ . The acetyl content (11.8%) agreed

with the value calculated on the basis that two out of nine hydroxyl groups originally present in starch resisted methylation and, on subjecting the acetate directly to the methyl sulphate reaction, the original material was regenerated (OMe = 36%).

Similarly, the use of diazomethane was ineffective in raising the methoxyl value, which remained remarkably steady in eight successive preparations of methylated starch (Found : OMe, 35.6; 35.4; 35.2; 36.3; 35.8; 35.2; 35.4; 35.5%). The specific rotation in chloroform also showed little variation, the extremes being  $[\alpha]_D +151.5^\circ$  and  $152.6^\circ$  for  $c = 1.25$ . These results point to the idea that methylated starch is a homogeneous definite compound, but it may be emphasised that the above specific rotation is greatly increased if in the preparation of the compound the methyl sulphate reaction is supplemented by treatment with silver oxide and methyl iodide. Typical examples are quoted :

Methylations.			
(a) With methyl sulphate.	(b) With methyl iodide.	$[\alpha]_D$ .	Solvent.
4 followed by	1	+168.1°	Chloroform.
4           "	3	169.5	"
5           "	2	173.9	"
4           "	3	186.2	Methyl alcohol.

Reasons exist for the belief that this alteration in rotatory power is attributable to depolymerisation.

#### *Hydrolysis of Methylated Starch.*

A 10% solution of methylated starch in methyl alcohol containing 1% of hydrogen chloride was kept at the boiling point until the activity was nearly constant. Initially, the solution was opalescent, but rapidly cleared so that accurate readings were possible. Some typical results are quoted below, the complete series giving a smooth, unbroken curve.

Time from start (hours) ...	2	3	5	6	7	8
$[\alpha]_D$ .....	+114.4°	+99.8°	+81.7°	+75.0°	+70.3°	+69.8°

The product, consisting of a mixture of methylated glucosides, was isolated in the usual manner and formed a clear viscous syrup. Practically the whole of the material dissolved in boiling ether and the syrup obtained on removal of the solvent was dried at  $100^\circ/1$  mm. Yield 21.8 g. from 23 g. of methylated starch.

The two components, *viz.*, trimethyl and dimethyl methylglucosides, were separated by a tedious method which need not be described as it has been superseded by a superior process. The trimethyl methylglucoside was finally distilled at  $120^\circ/0.7$  mm. as a colourless liquid ( $n_D$  1.4585) which crystallised. When purified

from light petroleum, the crystals melted at  $57^{\circ}$  and showed  $[\alpha]_D - 20^{\circ}$  in methyl alcohol (Found: C, 50.6; H, 8.5; OMe, 52.2. Calc. for trimethyl methylglucoside: C, 50.8; H, 8.5; OMe, 52.5%). The glucoside was converted into crystalline tetramethyl glucose by the usual processes, thus showing that it belongs to the stable type, and when hydrolysed with aqueous hydrochloric acid gave crystalline 2:3:6-trimethyl glucose in 94% yield (mutarotation in methyl alcohol  $+ 83^{\circ} \rightarrow 68.3^{\circ}$ . OMe, 41.8. Calc. for trimethyl glucose, 41.9%). A careful search for tetramethyl glucose and for 2:3:4-trimethyl glucose gave entirely negative results. The dimethyl methylglucoside fraction distilled at  $140^{\circ}/0.4$  mm. as a viscous liquid (Found: C, 48.6; H, 8.1; OMe, 42.0. Calc.: C, 48.6; H, 8.1; OMe, 41.9%). As the compound was unknown, it was examined in some detail. On complete methylation, it was converted into tetramethyl methylglucoside, the  $\beta$ -isomeride being present in excess, and when condensed with benzaldehyde it gave a benzylidene derivative. This crystallised imperfectly and could not be characterised definitely as the benzylidene dimethyl methylglucoside described by Irvine and Scott (J., 1913, 103, 575), although the similarity was very marked. Hydrolysis of the glucoside with aqueous hydrochloric acid gave the corresponding dimethyl glucose as a clear glass. This had the correct analytical composition and showed  $[\alpha]_D + 56.6^{\circ}$  in acetone solution, but the material failed to crystallise. The sugar formed no phenylosazone and did not condense with acid acetone, properties which further suggest that the compound was 2:3-dimethyl glucose, but oxidation with nitric acid under the conditions described by Haworth and Leitch (*loc. cit.*) gave a complex mixture. It was, in fact, the study of this reaction which directed our attention to the untrustworthy nature of such oxidations.

With regard to the yields of the glucosides obtained from methylated starch it is important to note that tetramethyl methylglucoside was absent and monomethyl methylglucoside was present to an extent not exceeding 5%. The ratio of the dimethyl to the trimethyl methylglucoside was 1.85:1, a result which shows that 2 molecules of the former were produced to 1 molecule of the latter (calc., 1.88:1). This was confirmed by repeating the complete series of experiments.

#### *Preparation of Trimethyl Starch.*

The methylation of starch may be carried to completion by continuing the methyl sulphate reaction in the manner now described. At the conclusion of the fourth methylation, when the reaction mixture was raised to  $100^{\circ}$  to destroy excess of methyl sulphate, the

liquid was saturated with salt. The hot liquor was then poured away, leaving the methylated starch adhering to the flask as a plastic mass. On adding hot water, a homogeneous syrup was gradually formed, and this was subjected directly to the next methylation, but at regular intervals the product was separated in a pure condition in order to ascertain with certainty the yields and analytical composition. The homogeneous aqueous syrup was therefore carefully neutralised with sulphuric acid and, after dilution with water, extracted by shaking with chloroform. The residue left on evaporation of the solvent was dried and taken up in dry chloroform, the solution being boiled for 20 minutes with charcoal and filtered hot. A hard, brittle material was left on removal of the chloroform and this, on boiling with ether, was converted into a white, amorphous powder. The treatment with ether eliminated traces of solvent and also removed a small quantity of depolymerised material. The following table indicates the progressive nature of the methylation :

No. of methylations .....	5	10	14	20	24
% OMe .....	35.5	39.6	41.4	43.2	43.7
$[\alpha]$ in $\text{CHCl}_3$ ( $c = 1.7$ ) ...	+173.9°	+196.8°	+204.8°	+207.2°	+216.5°

At each stage, the carbon and hydrogen values were consistent with the methoxyl content, thus showing that the methylation proceeded without molecular rupture.

Starting from 32 g. of starch, the average yield after ten methylations was 15 g. and thereafter the experimental loss was regular, amounting to less than 0.4 g. per treatment. The final product (10 g., m. p. 143—146°) was a white powder less soluble in hot water than in cold, insoluble in ether, readily soluble in chloroform and in methyl alcohol. The aqueous solution was neutral, had no action upon Fehling's solution and gave no coloration with iodine (Found : C, 52.6; H, 8.0; OMe, 43.75. Calc. for trimethyl starch : C, 52.9; H, 7.8; OMe, 45.6%).

#### *Hydrolysis of Trimethyl Starch.*

*Method (a). Uncontrolled Hydrolysis.*—An 8% solution of methylated starch in methyl alcohol containing 1% of hydrogen chloride was heated at 100° for 24 hours and thereafter at 130° for 12 hours. The solution, which remained practically colourless, was neutralised with silver carbonate, filtered, taken to dryness, and the residue dissolved in ether. On filtering and evaporating, a colourless syrup remained (yield 94% of the theoretical amount) which was distilled under 0.1 mm. pressure. As the first drops of the distillate showed  $n_D$  1.4551 and had OMe 51.4%, tetramethyl methylglucoside was definitely absent. The main fraction (yield

84%), which showed  $n_D$  1.4583 and OMe 51.9%, consisted of trimethyl methylglucoside, a small, undistilled residue (OMe, 44%) being left in the flask. As under the conditions of the experiment the methylated glucoside was a mixture of  $\alpha$ - and  $\beta$ -forms, it failed to crystallise (Found: C, 50.6; H, 8.4; OMe, 51.9. Calc. for trimethyl methylglucoside: C, 50.85; H, 8.5; OMe, 52.5%.  $[\alpha]_D$  in methyl alcohol + 69.8° for  $c = 1$ ).

The glucoside was thereafter hydrolysed by heating at 100° in 5% aqueous hydrochloric acid, the progress of the reaction, which was followed polarimetrically, displaying the characteristic double change in activity.

Time from start.	$[\alpha]_D$ for $c = 5$ .	Time.	$[\alpha]_D$ .
15 minutes.	+69.1°	3 hours.	+69.3°
45 minutes.	79.2	3 hours 45 minutes.	72.4
1 hour 45 minutes.	74.6	4 hours.	76.4
2 hours 30 minutes.	63.9		

The hydrolysis sugar, on isolation, crystallised immediately and completely, the m. p. before crystallisation being 70–80°, and, after purification from ether, 114°. This value remained unaffected on admixture with an authentic specimen of 2 : 3 : 6-trimethylglucose obtained from cellulose. The yield of crystalline sugar was 77% and the mother-liquors contained only a small quantity of uncrystallisable syrup. Contrary to expectation, this was not the isomeric 2 : 3 : 4-trimethyl glucose, as on conversion into the corresponding acetobromide and thereafter into trimethyl  $\beta$ -methylglucoside the product, after recrystallisation, melted at 57.5°. The compound also showed the correct mixed melting point and the standard specific rotation for 2 : 3 : 6-trimethyl methylglucoside.

*Method (b). Graded Hydrolysis.*—In this case, the hydrolysis was controlled so as to trace the stages of the reaction. The methylated starch (12 g.) was dissolved in 250 c.c. of methyl alcohol containing 1% of hydrogen chloride and boiled under a reflux condenser until the activity of the solution diminished to a minimum. This point was reached in from 8 to 9 hours and the product was isolated in the usual way. When distilled under 0.8 mm., 10.5 g. of pure trimethyl methylglucoside were obtained, whilst 2.8 g. remained undistilled. The distillate crystallised readily and, after purification from low-boiling petroleum, melted at 57.5° and showed  $[\alpha]_D -29.3^\circ$  in methyl alcohol for  $c = 1$ . When it was hydrolysed with 5% aqueous hydrochloric acid, the specific rotation altered from  $-25.4^\circ$  to + 59.5° in 200 minutes, and crystalline 2 : 3 : 6-trimethyl glucose was ultimately obtained, the yield being 82%. A portion of the trimethyl methylglucoside failed to crystallise, but this material, which presumably contained the  $\alpha$ -isomeride, was recovered from

the tile and hydrolysed separately. In this case also, 2:3:6-trimethyl glucose was the only sugar formed.

As already stated, 2.8 g. of non-volatile material were left undistilled when the hydrolysis of methylated starch was conducted as now described. The substance was a hard glass and consisted of depolymerised trimethyl starch (Found: C, 52.5; H, 8.0; OMe, 43%), as the composition remained unaltered but the solubility had increased while the specific rotation had diminished to  $+86.9^\circ$  in chloroform. Hydrolysis took place only when this material was heated for many hours at  $130^\circ$  with methyl alcohol containing 1% of hydrogen chloride, but the essential product was, as before, 2:3:6-trimethyl methylglucoside (OMe 41.6%;  $n_D$  1.4590). This, in turn, was converted into crystalline 2:3:6-trimethyl glucose, the identity of which was confirmed by transformation into the corresponding  $\beta$ -methylglucoside. No trace of the 2:3:4-isomeride could be detected.

The authors gratefully acknowledge their indebtedness to the Carnegie Trust for a Research Scholarship and a Research Fellowship which enabled one of them to devote 4 years to the investigation.

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## CXCVI.—*The Ultra-violet Spectra of Praseodymium, Neodymium, Samarium, Europium, and Erbium.*

By JAMES HENRY GARDINER.

VERY little work has been done in the photography of the ultra-violet absorption spectra of the rare earths, possibly on account of the rarity of the elements themselves and of the difficulty of photography.

Having in my possession specimens of many of the rarer elements in a state of purity, I thought that it would be of interest to place on record photographic reproductions of the absorption spectra of some of them. The five named above were found to give well-defined absorption bands in the region under examination; these spectra are shown together with a photograph of the light used to produce them. Photographs of this character lose much of their value unless care is taken to ensure uniformity in the conditions under which they are produced.

The spectrograph used is of novel design and has been constructed

purposely for this class of work; it consists essentially of a pair of quartz "Cornu" prisms with plano-convex collimating and object lenses. The "comparison spectrum" that is given in each case is put into position without any movement of the film by passing the radiation into the spectrograph through an aperture in a metal disc which is fixed in front of the slit; this disc has holes of different sizes and in different positions and it can be moved so as to confine the radiation entering the instrument to any one of them at will.

For this work it was necessary to use a very narrow slit, and it was essential for purposes of comparison that there should be no variation from the width in any of the spectra. A thick brass plate with a slot 2 mm. wide and 10 mm. long was made, and by the point, slot, and plane method it could be accurately fixed in the optical centre of the quartz train; upon the flat surface of the plate, jaws of hard steel with accurately ground edges were clamped at the determined width of 0.03 mm. This device of a slit with jaws that are immovable removes any possibility of accidental variation in its width such as would arise if it were adjusted by a screw.

All the photographs given are made with the same slit. The light used for the absorption spectra was produced by passing a high-tension current between electrodes of metallic uranium, producing a spark very rich in ultra-violet radiation. The spectrum of uranium has such a great number of lines so close together that, for the present purpose, it may be regarded as continuous.

At the top of each absorption spectrum and slightly overlapping it, is projected the spark spectrum of an alloy of the metals zinc, cadmium, mercury, and tin. These elements give well-defined lines of which the wave-lengths are known to a great degree of accuracy; their values given on each photograph make it possible, by means of a simple interpolation curve, to find the value of any of the bands shown. The wave-lengths of the approximate centres of the bands are given, although the photographs themselves are of more value than tables of wave-lengths and descriptions of the bands.

It was considered essential that the strengths of the solutions, *i.e.*, the amounts of the element present in each case, should be comparable or at least accurately known. The rarity of the materials available, and the obscurity of the chemistry of some of them, made this a matter of difficulty, but after some preliminary work it was decided to take the crystalline nitrates which have the general formula of  $R(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  as the basis of the solutions. These salts are easy to prepare and are soluble in water. As in some cases only a fraction of a gram of the element was available, it was decided to make all solutions from a weighed quantity of the

salt with ten times its weight of water. The solutions were in all cases put into a cell made from a glass cylinder, 20 mm. long, closed at the ends with plates of thin quartz.

The procedure for the production of a photograph was as follows. By adjusting the aperture-disc so that the light passed into the upper part of the slit, an exposure was made to the light from the metallic alloy, and the disc was then rotated so as to present another opening slightly overlapping the first; the cell containing the solution was fixed in front of the slit, an exposure was given for 3 minutes to the uranium spark, the disc was again shifted so as to expose another part of the slit, and the solution was removed and another exposure given to the same light for the same time; this last exposure was considered to be advisable for reasons that will appear later.

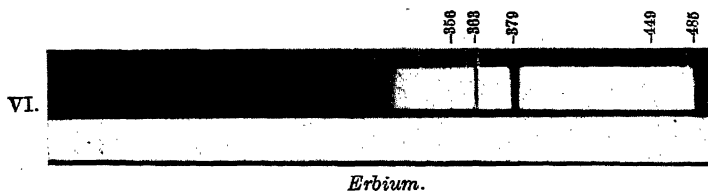
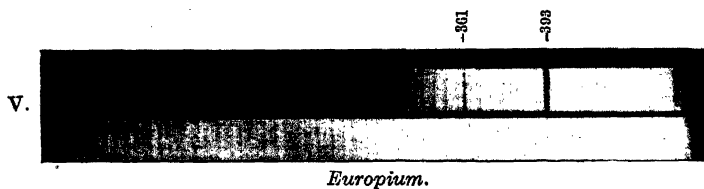
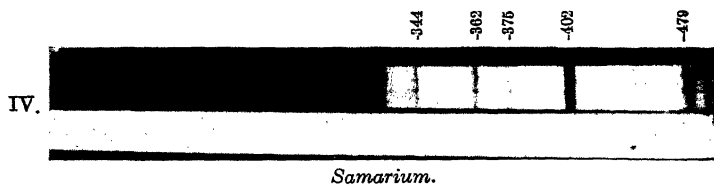
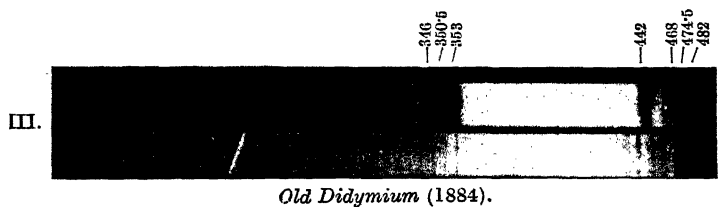
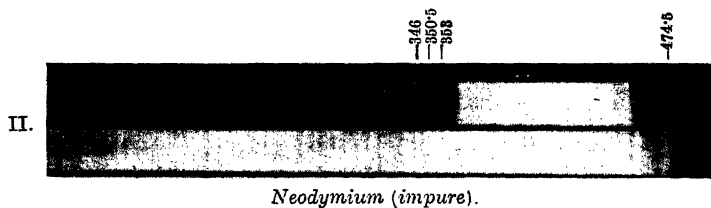
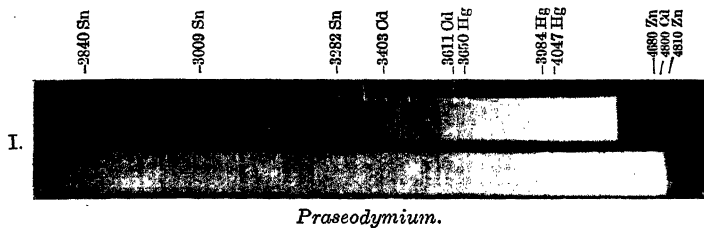
In addition to the five elements that form the subject of this paper, 1 : 10 solutions of the nitrates of the following elements were made and their absorption spectra were photographed: lanthanum, ytterbium, gadolinium, terbium, thorium, cerium, and scandium. They did not show any absorption bands in the region under examination, *i.e.*, from  $400\mu$  to the commencement of transmission, which in all cases was at about  $350\mu$ . The elements giving absorption bands are described in the order of their atomic numbers.

*Praseodymium.*—This specimen was prepared some years ago by Thompson. The nitrate gives well-defined crystals dissolving easily in water to a brilliant green solution; the dried crystals,  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , were used for the solution which was placed in the cell described above. The spectrum shows that it is quite free from neodymium and gives three well-defined bands at the least refrangible end; the approximate centres of the bands are  $482\mu$ ,  $468\mu$ , and  $442\mu$  (Fig. I).

*Neodymium.*—This material was obtained from the Welsbach Co. in the form of deliquescent crystals of pale rose colour; it was recrystallised by keeping the solution over sulphuric acid and gave good crystals of  $\text{Ne}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The spectrum (Fig. II) shows that the material is not quite free from praseodymium, but the three bands corresponding to this element are very faint; the bands of neodymium, however, are definite, and in this region of the spectrum are represented by a very faint and narrow band midway between the two least refrangible bands of praseodymium, at  $474.5\mu$ , and a well-defined group of three bands which do not appear to have been recorded hitherto; the wave-lengths of their maxima are approximately:

$353\mu$ . Centre of the strongest part of a band having a broad wing on its least refrangible side;





1

350.5  $\mu$ . Brightest edge of a band, fading off at the most refrangible edge;

346.7  $\mu$ . Centre of the most refrangible band.

An interesting confirmation of the allocation of the faint band at 474.5  $\mu$  to neodymium is seen by reference to Fig. III, which is the absorption spectrum of a 1 : 10 solution of the nitrate of a specimen of didymium prepared, in the form of a dark brown oxide, by Cleve in 1884—some 12 months before Welsbach announced his discovery of the complex nature of the substance. It can be seen that all the bands of praseodymium and neodymium are visible, including the faint one at 474.5  $\mu$ .\*

*Samarium.*—Samarium nitrate forms yellow crystals of  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The spectrum of its solution is characterised by a very strong band having sharp edges and by four other broad, but faint, bands; there is also an indication of a fifth band, but it is too faint to measure. As the spectrum as a whole did not seem to correspond to the description given by Demarcay (*Compt. rend.*, 1900, 130, 1185), other photographs of it were made using stronger solutions, but the character of the bands did not change. The measurements of the approximate centres of the bands are (Fig. IV) :

First faint band : 479  $\mu$ . Centre of dominant band : 402  $\mu$ .

Centres of other faint bands : 375  $\mu$ , 362  $\mu$ , 344  $\mu$ .

*Europium.*—This element is one of the rarest of the yttria earths. The oxide of the specimen under examination was of a faint cream tint, whereas it is said to be light pink. The spectrum shows a strong but narrow band with a very sharp edge on the more refrangible side, and one other faint but equally sharp band; the wave-lengths of the approximate centres are 393  $\mu$  and 361  $\mu$  (Fig. V).

Another specimen of this earth from an unknown source gave exactly the same spectrum.

*Erbium.*—The material from which the nitrate was prepared was a pink oxide prepared by Cleve in 1885. The wave-lengths of the absorption bands as determined by various observers vary considerably, but in this case there was one dominant band accompanied by four others that are all very faint; the wave-lengths of the approximate centres are as follows (Fig. VI) :

A strong band at 485  $\mu$ ; a very faint band at 449  $\mu$ .

\* In discussing the spectrum of neodymium, J. F. Spencer ("The Metals of the Rare Earths," 1919) states that a band with a maximum at 469  $\mu$  coincides exactly with one of the praseodymium bands and that this has led to the view that these substances contain an undiscovered element. The photographs of Cleve's old didymium and of the later praseodymium and neodymium fail to justify this view, as all the bands of the old element in this region of the spectrum are accounted for

The dominant band, sharp on the least refrangible side, at  $379\ \mu$ .

A very faint band, which is crossed by a strong uranium line (from the source of light), at  $363\ \mu$ .

A very faint line at  $365\ \mu$ .

This element is said to be slightly radioactive and a photographic experiment was therefore made: the oxide was filled into a tube closed at the end by a sheet of aluminium foil 0.04 mm. thick, which was fixed on a photographic plate so that the oxide was separated from the sensitive surface by the aluminium, and it was shut up in a dark box for 7 days. On developing, a faint but decided impression was obtained, where the oxide had rested. A similar experiment made with europia also gave an indication of radioactivity, but much more feebly.

[Received, January 27th, 1926.]

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## CXCVII.—*Extinction of Methane Flames by Diluent Gases.*

By HUBERT FRANK COWARD and FRANCIS JOHN HARTWELL.

IN the course of an investigation on the influence of black-damp (a mixture of nitrogen and carbon dioxide) on the limits of inflammability of firedamp (methane) in air (Safety in Mines Research Board, Paper No. 19; London, H.M. Stationery Office, 1926), some new information has been obtained concerning the factors which determine whether or not a gas mixture is capable of self-propagation of flame. Volume for volume, carbon dioxide exceeds nitrogen in its extinctive action on flame—an effect which is generally attributed to the higher molecular heat capacity of the former. Argon, a gas of lesser heat capacity than either, proves to have less extinctive action. On the other hand, helium is much more extinctive of flame than argon, although the two have almost exactly the same heat capacities.

The limits of inflammability of methane, in various "atmospheres," composed of mixtures of air with one or other of the diluent gases, were determined in a vertical glass tube, 6 feet long and 2 inches in diameter. This tube was filled with an appropriate mixture, the lower end was then opened by sliding away a ground-glass joint and a small spirit-lamp flame was immediately passed across the aperture. The tube was sufficiently long to enable observers to judge whether a flame was self-propagating; for, if the mixture were incapable of continued self-propagation

of flame, the "cap" of flame formed above the source of ignition was extinguished within 2 feet of its passage up the tube.\*

*General Observations on the Flames.*

The flame front, as the flame passed up the tube, was in all cases nearly hemispherical in shape, sometimes with a hollow, cylindrical extension of variable length. The blue flame front was followed by a red glow in all upper-limit mixtures, an evidence of some residual chemical reaction. The speed of propagation of flame in all limit mixtures, lower or higher, was remarkably constant at 22 to 23 cm. per second, except that the speed was somewhat higher when helium was the diluent used.

The flames in certain upper-limit mixtures vibrated rapidly when within 1 or 2 feet of the top of the tube. During these vibrations the flame, on occasion, was extinguished; however, when a pad of cotton wool was held loosely over the open end of the tube during the progress of the flame, vibrations were not observed and the normal shape of flame front and speed of propagation were obtained. Furthermore, the flame vibration started at the moment when the contraction due to cooling behind the flame became equal to, or just exceeded, the expansion due to new combustion; *i.e.*, at the moment of change, at the open mouth of the tube, from an outflow of gases to an inflow of air.

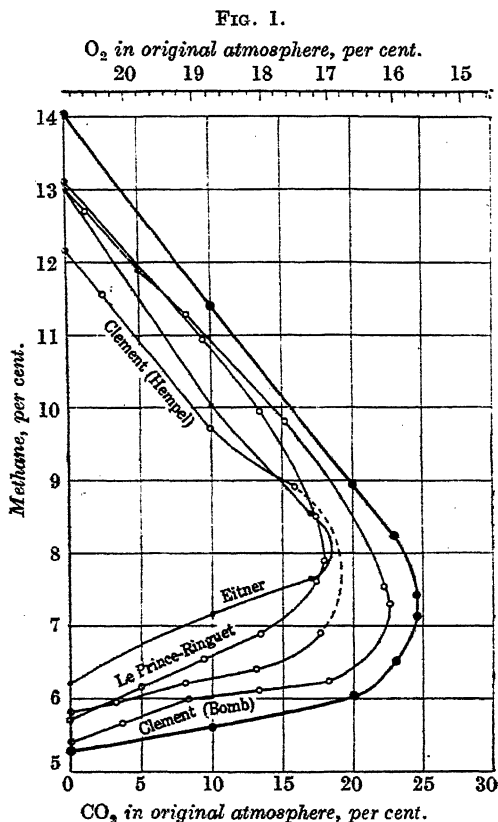
These observations afford a clue to an understanding of the causes of vibration in flames travelling along tubes, and will, it is hoped, form the subject of a later communication.

*Limits of Inflammability of Methane-Air Mixtures in the Tube Used.*—The limits in the circumstances described were 5.24% methane (lower) and 14.02% (higher).† These may be taken as accurate to 0.02%. Most of the results in the following sections were determined within 0.05%.

\* In all the experiments recorded here, the gases were roughly dried by passage over calcium chloride, and contained less than 0.1% of moisture. They were at laboratory temperature up to the time of inflammation, and at laboratory pressure during the whole time of passage of the flame; the latter condition was secured by leaving the lower end of the tube open while the flame was passing up the tube. Ordinary variations in laboratory temperature and pressure have no measurable effect on the limits of methane-air mixtures (Mason and Wheeler, J., 1918, 113, 45).

† When the gases were saturated with water vapour (1.9%) at the temperature of the experiment, the limits proved to be 5.22% methane (lower) and 13.54% (higher). These are the actual proportions of the gas present in the moist mixture; expressed (as usual from gas analyses) as percentages of the water-free mixture, they become 5.33 and 13.80. These last figures may be compared with earlier determinations which are, as a rule, expressed in this manner.

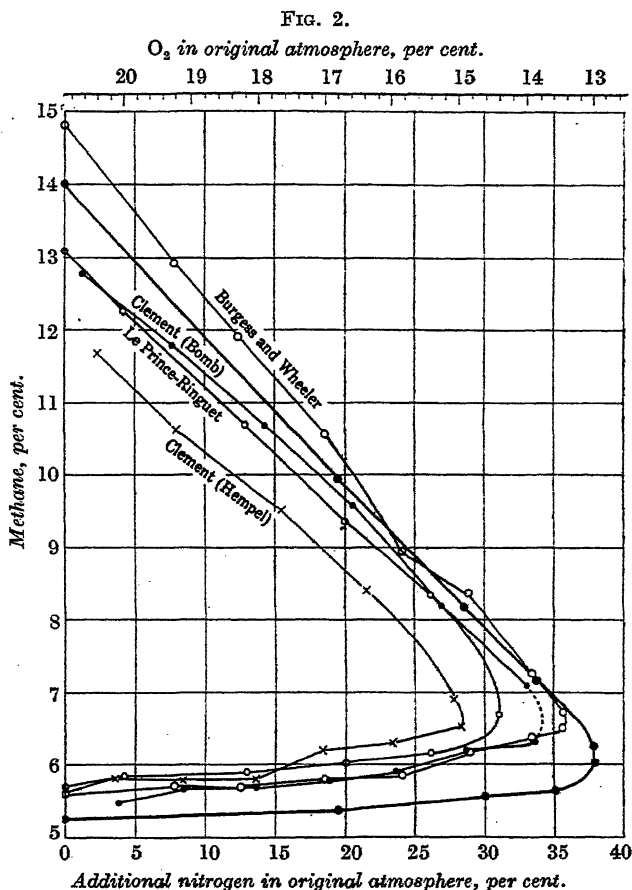
*Influence of Carbon Dioxide on the Limits of Inflammability of Methane-Air Mixtures.*—The heavy curve in Fig. 1 represents the limits of inflammability of methane in atmospheres composed of pure air admixed with the indicated amounts of carbon dioxide. The limits are narrowed as the amount of diluent gas is increased, until they meet when the atmosphere contains somewhat less than 25% of carbon dioxide. The increase in the lower limit is



apparently due to the greater thermal capacity of the carbon dioxide, whilst the decrease in the higher limit is due to the combined effect of this and of the reduction in oxygen content of the atmosphere.

In the same figure are plotted results obtained by Eitner (*Habilitationsschrift*, München, 1902), Clement (*U.S. Bureau of Mines*, 1913, Technical Paper 43), and Leprince-Ringuet (*Compt. rend.*, 1914, 158, 1999). They are not strictly comparable, however,

for the conditions of experiment were somewhat different in each case. Thus Eitner's and Leprince-Ringuet's refer to experiments on the downward propagation of flame in these mixtures, and Clement's to the propagation from a point near the top of a Hempel burette, or of a steel cylinder of some 3 litres capacity. The wider



limits indicated by our experiments, in which upward propagation was observed, were therefore to be expected.

*Influence of Nitrogen on the Limits of Inflammability of Methane-Air Mixtures.*—The heavy curve of Fig. 2 represents correspondingly the limits of methane in atmospheres composed of pure air admixed with the indicated amounts of nitrogen. The extinctive effect of nitrogen is considerably less than that of carbon dioxide, for the two limits do not coincide until about 38% of added nitrogen

is present in the atmosphere, as compared with 25% of carbon dioxide. These figures are almost exactly in the inverse ratio of the mean molecular heats (at constant pressure) of the two gases between room temperature and the flame temperature. Hence the difference in extinctive action is doubtless due to the difference in heat capacities of the two diluents. The lower limit shows a small but definite rise with increase in the proportion of nitrogen. As this diluent has the same heat capacity as air up to, and beyond, the flame temperatures of these experiments, this small rise must be ascribed to the reduction of the oxygen content of the atmosphere. The effect is masked by the operation of other factors when other chemically inert diluents are used.

Fig. 2 shows also the results of Clement (*loc. cit.*), Leprince-Ringuet (*loc. cit.*), and Burgess and Wheeler (J., 1914, 105, 2596). Here, again, the results are not closely comparable with the present series, for they were obtained under different conditions; but whereas for carbon dioxide-air "atmospheres" all the previous results showed narrower limits than those now presented, one set of the nitrogen results (Burgess and Wheeler's) shows, in general, greater values for the higher limits. Now those experiments were conducted in closed vessels, wherein the pressure rose considerably (several atm.) during the inflammation, and Mason and Wheeler (J., 1918, 113, 45) have shown that increase of pressure increases markedly the higher limit of methane-air mixtures.

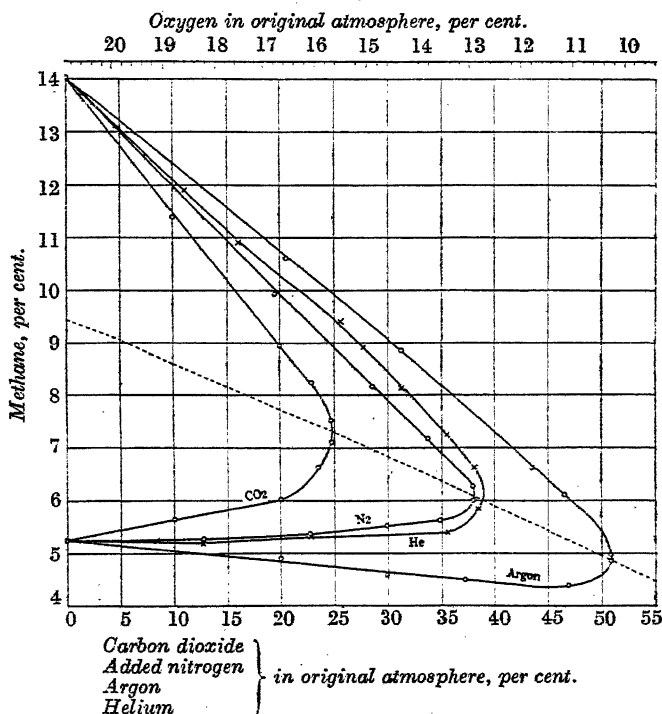
*Influence of Argon on the Limits of Inflammability of Methane-Air Mixtures.*—If the conclusions drawn from the experiments with atmospheres containing carbon dioxide and added nitrogen are correct, the lower limit of methane will have smaller values in atmospheres made from air and argon than in air itself, for argon has a lower heat capacity than air. Fig. 3 shows that such is the case, and that the minimum value of the lower limit is 4.40% of methane in an atmosphere composed of about 47% of argon and 53% of air, as compared with 5.24% of methane in the case of pure air. It requires nearly 51% of argon in admixture with air to produce an atmosphere which cannot form an explosive mixture with methane.

*Influence of Helium on the Limits of Inflammability of Methane-Air Mixtures.*—The heat capacity of helium is very nearly equal to that of argon and each, apparently, remains constant up to high temperatures. If, therefore, the extinctive effect of an inert gas is solely due to its thermal capacity and to its effect on the oxygen concentration of the atmosphere, the limits of methane should be identical in atmospheres composed of ordinary air mixed in one case with argon and in another case with an equal volume



of helium. Fig. 3 shows the action of helium, which, contrary to expectation, is markedly more extinctive of methane-air flames than is argon.\* From a detailed consideration of the physical differences between these two gases, we ascribe the superior extinctive action of helium to its greater thermal conductivity,† which is more than eight times that of argon, at laboratory temperatures. We have no experimental information about the temperature coefficients of the conductivities of such mixtures as we are using,

FIG. 3.



\* A mixture of composition  $\text{CH}_4 + 2\text{O}_2$  was diluted with (a) argon, (b) helium, until it was no longer inflammable. The limit mixtures contained (a) 3.95, (b) 5.00% methane. For downward propagation of flame in a tube of the same size, firing from near the open end, similar results were obtained; in an atmosphere composed of 80% of air and 20% of inert gas, the lower limits were (a) 5.50, (b) 5.75% methane when the inert gas was (a) argon, (b) helium.

† The thermometric conductivity, or diffusivity, which is equal to the thermal conductivity divided by the specific heat ( $C_p$ ) of unit volume, is the function which would have to be used in a quantitative analysis of the phenomena of flame transmission. In the present argument, the terms may be used interchangeably.

but some indication is given by Stafford's work (*Z. physikal. Chem.*, 1911, 77, 66) on the temperature coefficients of the conductivities of air and carbon dioxide separately, and Weber's work (*Ann. Physik*, 1917, 54, 481) on the conductivities of some mixed gases at laboratory temperatures. It seems highly probable that the thermal conductivity of a gas mixed with helium will be greater than that of a corresponding mixture with argon, and that this will be true at the somewhat high temperatures of the flames in limit mixtures. At first sight, it is surprising that the higher thermal conductivity of helium should be responsible for its greater extinctive action; but if the propagation of flame is due to conduction of heat, then at either zero or infinite values of the thermal conductivities flame would not be propagated. Between the two values, zero and infinity, an optimum value for the conductivity must obtain; so it is evident that the higher conductivity of the helium mixtures may well be less favourable to flame propagation in limit mixtures than the lower conductivity of the argon mixtures.

This conclusion is in good accord with, and receives support from, observations made by Coward, Cooper, and Jacobs (*J.*, 1914, 105, 1069). They found that it was much more difficult to ignite, by the electric discharge, mixtures of various gases when diluted with helium than when argon was used, and they interpreted the results in a similar manner.

#### *General Discussion.*

If, therefore, it is probable that the differences between the argon and helium curves are due to the different thermal conductivities of the two gases, it is necessary to consider how far the discovery of the influence of this factor may affect our previous conclusions as to the influence of varying heat capacities.

The thermal conductivities at 0° of the gases under consideration are (Glazebrook, "Dictionary of Applied Physics," 1922, vol. 1, p. 459)

Helium .....	$32.7 \times 10^{-3}$	Nitrogen .....	$5.14 \times 10^{-3}$
Argon .....	3.85 "	Air .....	5.22 "
Carbon dioxide .....	3.25 "		

The difference in thermal conductivity between carbon dioxide and nitrogen (1.9 units) seems far too small to account for the difference in extinctive action between these two gases, for there is about the same difference in extinctive action between helium and argon for a very much greater difference in thermal conductivity (28.9 units). We may therefore adhere to our earlier conclusion that the thermal capacity factor is predominant in determining the relative extinctive effects of two diluent gases, but we may

add that, when a gas of very different thermal conductivity is introduced, then this factor will become important.

*A Connexion between Lags on Ignition and Dilution Limits.*—When inflammable mixtures of methane and air are heated to any temperature above their ignition temperature, a distinct interval of time must elapse before inflammation is observed. The relative ease of ignition of methane-air mixtures containing the various diluents used in this research, as indicated by their relative "lags" on ignition, might be regarded as a governing factor in determining the order of the limits. Determinations of such "lags" have recently been made in the Safety in Mines Research Board Laboratories in connexion with another research which will be published shortly. At the temperature of the flames in limit mixtures (calculated to be between 1100° and 1400°) the lags, under the conditions of experiment, were too short to be measured for comparative purposes, but at 950° they were reasonably long, and are shown for 6% methane mixtures in atmospheres containing 30% of diluent. The same table also shows the limiting proportion of the diluent which is completely extinctive at normal temperature and pressure.

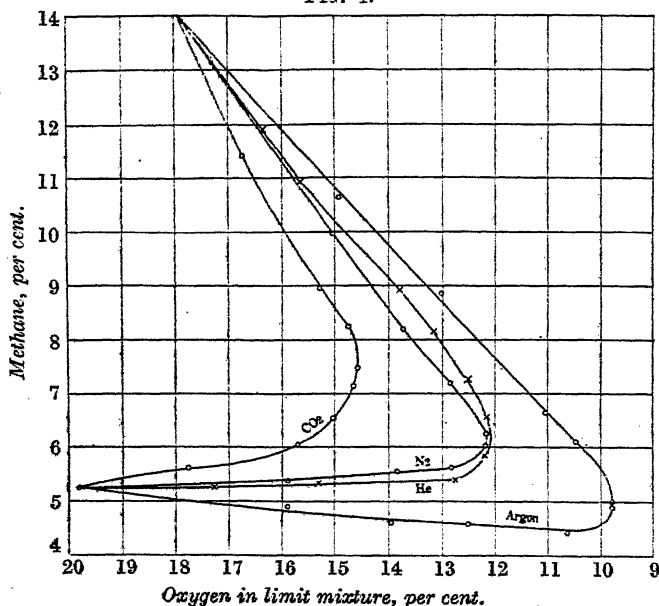
Diluent.	Carbon dioxide.	Nitrogen.	Helium.	Argon.
Lag (seconds) .....	0.275	0.25	0.22	0.19
Limiting proportion (%) ...	25	38	39	51

It is tempting, perhaps, to explain the relative extinctive effects as being the result of the relative lags; but it is more reasonable to regard the lags as determined largely by the same factors as determine the extinctive effects, namely, thermal capacities and thermal conductivities, because the lag is generally explained as being the period in which the gas mixture is heating itself, by partial combustion, to the temperature of rapid reaction. Other circumstances being equal, the lag must therefore be shorter in the presence, not only of inert gases of lower thermal capacity, but also of gases of lower thermal conductivity.

*The Most Inflammable Mixture of Methane and Air.*—The broken line in Fig. 3 is the locus of mixtures in which the ratio between methane and oxygen is exactly that required for complete combustion,  $\text{CH}_4 : 2\text{O}_2$ . This line runs through the "noses" of the limits curves, and therefore, from this point of view, the most inflammable of all mixtures of methane and oxygen is that which burns completely to carbon dioxide and water. This is also the mixture in which the speed of uniform movement of flame is greater than in any other mixture of methane and oxygen (Payman, J., 1920, 117, 48). On the other hand, the detonation wave is pro-

pagated more rapidly in mixtures in which the methane content exceeds that required for complete combustion (Dixon, *Phil. Trans.*, 1893, **184**, 97); in this case, the heat of reaction is evidently subordinated by those physical properties of the explosive mixture which govern the rate of transmission of a disturbance like a sound wave. Moreover, the speed of uniform movement of flame in methane-air mixtures reaches its maximum when the proportion of methane is somewhat higher than the theoretical amount for complete combustion (Wheeler, J., 1914, **105**, 2606), whilst mixtures

FIG. 4.



containing an excess of air are more readily ignited by a heated surface or by an electric spark.

*Test of the "Limits Generalisation" of Payman.*—Le Chatelier (*Ann. Mines*, 1891, **19**, 388) gave a formula which enabled the lower limit in air of a mixture of two inflammable gases to be calculated from the observed limits of the separate gases. This formula was put in more general form by Coward, Carpenter, and Payman (J., 1919, **115**, 27) and was shown to apply to lower and higher limits, in air, of mixtures of hydrogen, methane, and carbon monoxide, and of coal gas. It expressed in mathematical terms the statement that "lower-limit air mixtures, if mixed in any proportions, give rise to mixtures which are also at their lower limits."

Payman (J., 1919, 115, 1436) gave the statement a still wider form which applies to cases in which the atmosphere is not air: "All mixtures, in any proportions, of limit mixtures remain limit mixtures . . . provided that all of the limit mixtures are of the same kind, that is to say, all lower-limit or all upper-limit mixtures." This statement is tested by the present research for atmospheres which contain large quantities of carbon dioxide, excess nitrogen, argon, and helium. It holds good in each case when mixtures represented by points on the straight part of a curve (Fig. 4) \* are considered; it fails when points on the curved parts are considered, and the extent of the failure is represented by the greater or lesser curvatures at the point chosen. The generalisation is therefore fairly accurate for methane in atmospheres composed of air mixed with the inert gases named, except when applied to those mixtures the composition of which approaches the point where the lower and higher limits coincide.

### Results.

Limits of inflammability of methane in atmospheres composed of air mixed with various diluent gases, observed in a vertical tube 2 inches in diameter, upward propagation of flame, the lower end of the tube being open; gases at atmospheric temperature and pressure.

Diluent in "atmosphere"	Limits of inflammability.		Diluent in "atmo- sphere" %.	Limits of inflammability.	
	Lower.	Higher.		Lower.	Higher.
Nil.	5.24	14.02	Nitrogen.		
			19.6	5.39	—
Carbon dioxide.			19.8	—	9.97
10.0	5.61	11.40	28.5	—	8.18
20.0	6.07	8.95	30.0	5.55	—
23.0	6.57	8.23	33.8	—	7.18
24.5	7.12	7.47	35.0	5.63	—
Argon.			37.9	6.01	6.26
20.0	4.91	—			
20.6	—	10.62	Helium.		
29.9	4.60	—	12.8	5.27	—
31.3	—	8.85	16.0	—	10.90
37.2	4.48	—	22.8	5.35	—
43.6	—	6.62	25.6	—	9.40
46.6	—	3.11	27.7	—	8.93
46.9	4.40	—	31.3	—	8.14
50.8	4.87	—	35.3	—	7.27
50.9	—	4.99	35.5	5.40	—
			38.2	—	6.56
			38.5	5.83	—

\* The replotting of the experimental values on a different basis from that of Fig. 3 is necessary to exhibit the approach to a rectilinear character which tests the validity of the generalisation.

*Summary.*

1. The limits of inflammability of methane in atmospheres composed of air mixed with (a) carbon dioxide, (b) nitrogen, (c) argon, and (d) helium have been determined, and the factors which are mainly responsible for the extinction of flame have been elucidated. They are (1) the reduction of oxygen content by the diluent gas, (2) its thermal capacity, and (3) its thermal conductivity. An exact treatment of the subject would therefore demand a knowledge of the thermal conductivities of certain mixed gases up to high temperatures (say,  $1000^{\circ}$  to  $1500^{\circ}$ ). Such data are not at present available.

2. The thermal capacity effect of the diluent gas is marked in the case of argon; the lower limit of methane in the conditions described is reduced from 5.24% in air to 4.40% in an atmosphere composed of 47% of argon and 53% of air, and is further reduced to 3.95% in an atmosphere composed of argon with just sufficient oxygen to burn the methane completely.

3. The thermal conductivity effect is marked when a comparison is made between the limits in atmospheres composed of air to which has been added argon, on the one hand, or helium on the other.

4. The "limits generalisation" of Payman holds fairly accurately over the whole range of mixtures investigated, except near the point at which the lower and higher limits meet.

5. Of all mixtures of methane and oxygen, that represented by the proportions  $\text{CH}_4 + 2\text{O}_2$  is the last to become non-inflammable as inert gases (nitrogen; or nitrogen with carbon dioxide, argon, or helium) are added in increasing amount.

6. There is a parallel between the "lags" on ignition and the dilution limits of such mixtures as we have used. It is suggested that both are dependent on the same factors, in the case of any one inflammable gas.

This work has been carried out at the suggestion and under the general direction of Professor R. V. Wheeler. We desire to express our appreciation of the able manner in which Miss E. H. M. George-son and Mr. G. W. Jones, at Sheffield and Pittsburgh, respectively, have assisted us in this investigation, and to acknowledge the permission granted by the two organisations concerned to publish this work.

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CXCVIII.—*Periodic Phenomena at Anodes of Copper and Silver.*

By ERNEST SYDNEY HEDGES.

THE only case of the periodic dissolution of a metal under anodic polarisation which has received systematic examination is the periodic passivity of iron. A complete series of references to this and other periodic electrochemical phenomena is to be found in a paper by Hedges and Myers (J., 1925, 127, 1013). In that paper, periodic electrochemical phenomena were classified in two groups: (a) systems which are capable of furnishing a periodic current, and (b) systems which behave periodically on electrolysis; and the experimental portion was devoted to section (a). The present work is an experimental investigation of section (b).

The reactions differ in several important respects from the experiments of Hedges and Myers (J., 1924, 125, 604; 1925, 127, 445) on the periodic dissolution of metals in various reagents in absence of applied current. For example, a metal which liberates hydrogen when dissolving in an acid may undergo electrolytic dissolution without production of any gas, or at suitable current densities oxygen may be evolved at its surface. The absence of gas evolution enables diffusion effects, supersaturation, and film formation to play important rôles, and the system may be further complicated by polarisation, overvoltage, etc.

It is not surprising, therefore, that the electrolytic periods described in the present paper should differ in some fundamental respects from the periodic phenomena in purely chemical reactions. Thus, the periods formerly described were (1) dependent on the presence of a third component, (2) dependent on a peculiar physical state of the metal, (3) increased in frequency linearly with the rate of dissolution, and (4) lengthened enormously or stopped altogether by catalytic poisons. On the other hand, the electrolytic periods now described are (1) independent of a third component, (2) independent of the state of the metal, (3) decreased in frequency with increasing rate of dissolution, and (4) unaffected by catalytic poisons.

There are reasons for supposing, however, that the fundamental causes of these manifestations of periodicity are not essentially different.

## EXPERIMENTAL.

*Apparatus.*—The electrolysis was conducted in a wide-necked glass bottle of 200 c.c. capacity, the amount of solution used in each experiment being 100 c.c. The electrodes were of pure electro-

lytic metal sheet, 4 cm.  $\times$  2 cm., and were supported by nickel rods, to which they were fastened by means of a nickel screw, a small hole being drilled near the end of each electrode. A length of only 3 cm. of electrode was immersed in order to keep the nickel well clear of the solution. The metals were approximately 0.5 mm. thick, and the effective area of each may therefore be taken as 12 sq. cm. The distance between the electrodes was 2 cm. A rubber bung, closing the reaction vessel, served to carry the electrode supports and the glass tubes for stirring the solution. Except in experiments where it was undesirable, the solutions were vigorously stirred during electrolysis by a stream of air previously freed from carbon dioxide. The reaction vessel was immersed in a thermostat at 30°, except in those experiments where other temperatures are indicated.

The source of current was a battery of twelve Edison storage cells of large capacity. The current passing through the circuit was read directly on an ammeter placed in series with the cell, and the *P.D.* between the electrodes was measured by a voltmeter of suitably high resistance placed across the electrode terminals. Both were quite dead-beat instruments. The course of the electrolysis was followed by taking readings of the voltmeter every 15 seconds, or, if necessary, every 5 seconds.

#### (1) *Copper Anode.*

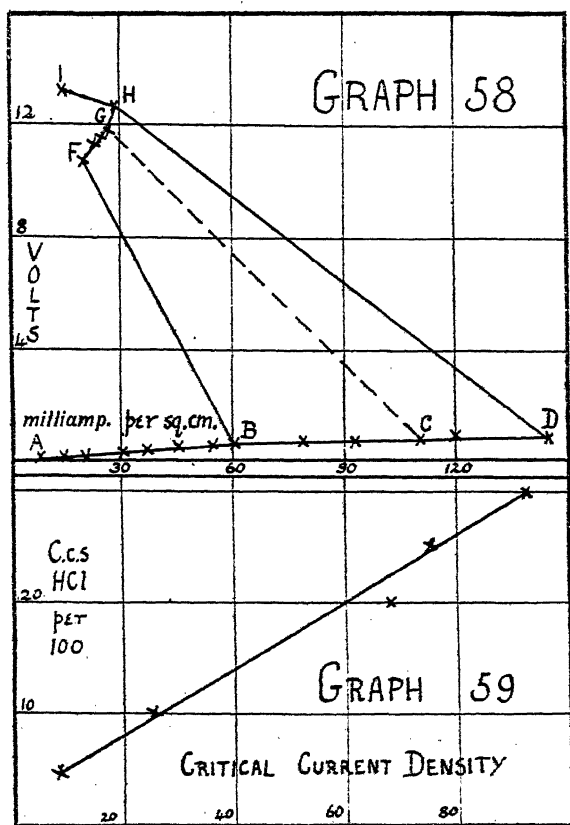
*Electrolysis of some Chloride Solutions.*—When fairly strong solutions of hydrochloric acid are electrolysed between copper electrodes at low current densities, copper passes into solution at the anode as cuprous chloride. As a rule, this may be seen on the metal as a white coating which, however, does not appreciably impede the electrolysis. In the absence of atmospheric oxygen, no cupric salt is formed. At high current densities, a film which appears to be cuprous oxide forms over the metal; this film is highly resistant and the current passing falls to a low value; the electrode still dissolves, but a small portion of the current is employed in the liberation of oxygen, a few bubbles of which rise from the anode. At intermediate current densities the two effects alternate. The seat of this phenomenon is the anode, for the effect continues if platinum be substituted for the cathode, but not if the anode be changed for another metal. Further, the anode undergoes a visible periodic change.

*The Current Density-Potential Curve.*—Graph 58 (Fig. 1) shows the effect of gradual increase in current density in the electrolysis of hydrochloric acid, containing 25 c.c. of acid (*d* 1.16) in 100 c.c., using a copper anode and a platinum cathode at 20°. For values



below 60 milliamp. per sq. cm. the potential rises slowly along the line AB: cuprous chloride is formed at the anode and dissolves in the hydrochloric acid, and at the cathode copper is deposited and hydrogen evolved. At the value corresponding to B the potential oscillates in regular periods between 0.55 and 10.6 volts, and simultaneously the current fluctuates between 60 and 20

FIG. 1.

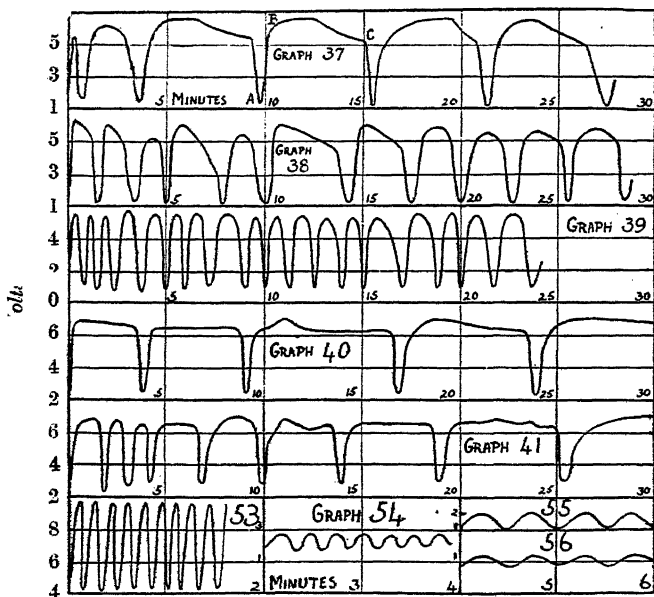


milliamp. per sq. cm. The region of regular oscillations continues as the current density is increased along BD to the value 145 milliamp. per sq. cm., the amplitude here being from 1.0 to 12.7 volts. At an intermediate point C, the values of current density and potential oscillate between points C and G. At current densities greater than 145 milliamp. per sq. cm., the potential immediately rises (the current falling) to a voltage corresponding to H, at which it remains constant. Further attempts to increase the current are

unsuccessful, for the film over the anode becomes more and more resistant and the effect is actually to decrease the current still further, along the line HI. The electrode, therefore, exists in one state along AB, in another state at H, and the area BFHD marks a region of instability where the electrode oscillates regularly between the two states.

The point B represents the critical current density required to produce periods. The value of this increases with the concentration of the hydrochloric acid and with rising temperature. The

FIG. 2.



The amplitude in Graphs 37—41 is about half of that indicated in Graph 58. This is because half the number of cells was used in these experiments. When the highly resistant film forms, the voltmeter records almost the total E.M.F. of the battery, the resistance of the rest of the circuit being relatively small.

critical current densities for a series of solutions containing from 5 to 30 c.c. of hydrochloric acid per 100 c.c. of solution electrolysed between two copper electrodes have been determined, and Graph 59 indicates a direct proportionality between critical current density and concentration.

#### *The Nature of the Phenomenon.*

The periodic changes in current and potential are accompanied by visible periodic changes at the anode. This is best described by reference to one of the waves on Graph 37 (Fig. 2). Simul-

taneously with the sudden rise in the potential (AB), there sweeps *up* the metal a very thin, dark grey film. The current slowly increases until the point C is reached. Then the potential rapidly resumes its initial low value and a white film sweeps *down* the metal. There is an interval of a fraction of a second between the drop in potential and the appearance of the white film. Careful observation shows that simultaneously with the drop in potential the smooth dark grey film breaks up into a rough red-brown film having the appearance of cuprous oxide. The transformation to the white film is almost immediate. The series of changes is repeated in each successive wave. The first film has the appearance of cupric oxide rather than cuprous, but there is doubt in assigning a composition to so thin a film. It is believed to be a form of cuprous oxide, for it changes directly into ordinary cuprous oxide and gives cuprous chloride by reaction with hydrochloric acid: further, no cupric salt is produced in the reaction. The white film is undoubtedly cuprous chloride.

It has been observed that wherever deposition of a film occurs in electrolysis, this starts at the sides and lower part of the electrode and travels up the electrode in the form of a U of diminishing concavity. This seems to be due to the concentration of current density at the corners and edges of the electrode and accounts for the manner in which the dark oxidic film travels up the anode. The downward sweep of the cuprous chloride film has been traced to the flow of hydrochloric acid down the electrode due to the downward fall of the reaction products, which is observed even when the solution is stirred. By allowing a stream of air bubbles to impinge on a point near the bottom of the anode, the reaction products can be washed upwards, and under these conditions the cuprous chloride film travels upwards also; but the oxide film could not be made to travel downwards.

The phenomenon is not affected by moderate rates of stirring, but when the solution in the vicinity of the anode is stirred very vigorously the frequency of the periods is increased or the potential may even remain constant at the low value. In the latter case, periodicity recurs on increasing the current density. Thus the phenomenon may be localised by directing a stream of air bubbles on a point about half-way up the electrode. In this case, the small area of metal affected by the rapid stirring exhibits rapid black and white flashes, while the main part of the electrode performs its slow periods unhindered. The voltmeter records curves showing short waves superimposed on the long waves.

These effects, which could be controlled by the air used for stirring, suggested that the phenomenon was due to oxidation and

probably to an oscillation of the reaction product between the cuprous and cupric states. Experiments were therefore performed in which the solutions were stirred by a stream of hydrogen bubbles. The effects of localised stirring were the same as with air and in this case no cupric salt was formed. Further, the periods were produced when the hydrochloric acid contained 1% of sulphurous acid. Separate experiments showed that a copper anode did not give periods in 1% or 5% sodium hydrogen sulphite solution alone. It may be noted that in the presence of sulphurous acid a somewhat higher critical current density was required.

Observations taken on interrupting the periods have given a clue to their nature. If the circuit be broken or the electrodes be short-circuited while the high *P.D.* exists, the cuprous chloride film immediately forms over the anode. In this case, it does not travel down the metal, but appears simultaneously over the whole area. If the circuit be completed again directly, the oxide film is reinstated immediately and the *P.D.* again rises. When an interval of 1 or 2 seconds elapses before the circuit is remade, the film does not form again for a few seconds. By breaking and making the circuit several times in succession, preferably in an unstirred solution, the cuprous chloride film does not form when the *P.D.* drops, but, instead, the oxide film turns to the red colour and the white film appears when the circuit is again made; it is quickly followed by the oxide film, the *P.D.* rising once more.

These facts suggest the following interpretation. The critical current density is such that chlorine ions are discharged more rapidly than they can be replaced by diffusion; at a certain moment, therefore, hydroxyl ions are discharged and a highly resistant oxide film forms over the metal, causing the *P.D.* to rise to a high value. This film is unstable (as will be shown independently later) and changes to a stable state of relatively low resistance, the change being indicated by the change in colour and surface of the film. This is immediately followed by reaction with the chlorine ions, which have been accumulating through diffusion, to form cuprous chloride. When the current is broken for a fraction of a second, the oxide film (which is only stable at the high potential) immediately reacts with the available chlorine ions and then rapidly forms again as these become scarce. When, however, the circuit remains open for a few seconds, the chlorine ions have time to diffuse towards the anode and, on making the circuit once more, a few seconds elapse before the oxide film forms. By repeating this process several times in rapid succession, the solution in the immediate vicinity of the anode can be so deprived of chlorine ions that breaking the circuit causes the highly resistant film to change to

the red stable state, in which form it persists for some little time; but closing the circuit causes it to react to form cuprous chloride.

Direct evidence of the instability of the highly resistant oxide film is gained by observing the effect of partially lifting the anode out of the solution when in the state represented by H in Graph 58. When this is raised 1 cm., the change to the stable state is observed to take place in the upper part of the electrode and a well-defined ridge forms about 0.5 cm. above the surface of the solution, marking the boundary between the stable and unstable forms. Each time the electrode is progressively raised, a further area remote from the solution undergoes the change and a new boundary forms, below which the grey film persists. This boundary marks the extent of the electrode which is under the influence of the high current density. The highly resistant film is stable, then, above a current density of 145 milliamp. per sq. cm., and its metastability between the values 60 and 145 milliamp. per sq. cm. is the cause of the periodicity.

Having deduced the mechanism of the process from direct experimental observation, it is necessary to show how this is supported by a study of the effect of varying the conditions of reaction.

#### *Effect of Conditions.*

(a) *Current Density.*—For any given concentration, the frequency of the periods decreases greatly with increasing current density. This is illustrated by the following values in a solution containing 25 c.c. of hydrochloric acid per 100 c.c.

Milliamp. ....	58	72	86	117
Min. ....	1.25	2.0	4.25	9

Such a result is to be expected, for the high current density (1) more rapidly exhausts the anolyte of chlorine ions, and (2) stabilises the resistant film.

(b) *Temperature.*—At a given current density, the frequency of the periods increases with rising temperature. This effect takes place in a particular way, however. The lower part of the curve (Graph 37) is unaffected and only the portion BC is shortened. On raising the temperature still higher, the amplitude AB is gradually reduced until finally the effect dies out and the potential remains constant at the low value. Periodicity can then be recovered by increasing the current density. Thus, a system at 20° under a current density of 80 milliamp. per sq. cm. gave an amplitude of 5.7 volts, the high *P.D.* lasting for 120 seconds; at 35°, the amplitude was 4.8 volts, lasting for 30 seconds; at 45°, 2.8 volts for 10 seconds; at 55°, 0.3 volt for 5 seconds. In each case, the low *P.D.* had a duration of 30 seconds.

Above  $60^{\circ}$ , no oscillation was perceptible, but by increasing the current density to 108 milliamp. per sq. cm. variations between 0.4 and 0.8 volt were recorded; at 126 milliamp. per sq. cm. the *P.D.* oscillated between 0.5 and 4.1 volts.

Thus, the effect of raising the temperature is to decrease the stability of the resistant film, and in every way it acts in an opposite sense to increasing current density: the two are mutually antagonistic.

(c) *Concentration*.—Graphs 37, 38, and 39 (Fig. 2) show that for a fixed temperature and current density (in this case  $30^{\circ}$  and 71 milliamp. per sq. cm.) the frequency of the periods increases with increasing concentration of hydrochloric acid. The rate of dissolution of the metal remains the same in the three cases. This result would be anticipated from the explanation advanced, for the anolyte is with greater difficulty depleted of its store of chlorine ions. The linear relation between the critical current density and the concentration of solution is likewise compatible. The wave-length gradually increases during the course of the electrolysis. This is due partly to decrease in concentration of the chlorine ions and partly to formation of cupric chloride through oxidation by the air-stream. Direct addition of 1% of cupric chloride was found to double the length of the waves.

(d) *Rate of Stirring*.—This factor is inconsiderable when the solution is kept in circulation without violently disturbing the solution at the anode. When the stream of bubbles is allowed to travel up the anode the frequency of the periods is increased and the critical current density raised. This is due to the rapid replenishing of the depleted chlorine ions, causing the effective concentration to be higher.

(e) *Addition of Agents*.—Addition of a reducing agent, such as sulphurous acid, served to shorten the periods and to raise the critical current density. On the other hand, oxidising agents such as hydrogen peroxide lengthened the periods. A system with a normal period of 4.25 mins. produced periods of 4.5 mins. after addition of 1 c.c. of 20-volume hydrogen peroxide, 6.5 mins. in the presence of 2 c.c. of hydrogen peroxide, and 10.5 mins. with 4 c.c. Addition of 0.5% of potassium cyanide or 0.5% of formaldehyde failed to "poison" the oscillations. The presence of 0.02% of gelatin did not affect the phenomenon. No difference could be observed between the behaviours of cold-rolled and well-annealed copper.

The periodic phenomenon takes place in solutions of other chlorides in similar circumstances and the same general effects are observed. Thus, equally well-marked periods are produced when

10% or 5% ammonium chloride is used for the solution to be electrolysed. Graph 40 (Fig. 2) illustrates the periodic dissolution of a copper anode in 5% ammonium chloride solution. Graph 41 records a similar experiment using 5% sodium chloride solution. In the latter case, the reaction product is mainly cuprous oxide, which is insoluble but does not adhere to the electrode; it soon causes the solution to become opaque, thus preventing observation. Long periods are obtained when 5% cupric chloride solution is used as the electrolyte.

#### *Electrolysis of Potassium Cyanide Solutions.*

Anodes of copper in 2.5% and 5% solutions of potassium cyanide rapidly become enveloped by a golden-green film which readily dissolves in the electrolyte on breaking the circuit. This is generally described as a basic cyanide. At certain current densities, the voltmeter needle trembles violently and occasionally executes rapid fluctuations of about 1 volt. The phenomena are much more definite in a 10% solution. At low current densities, no film forms over the anode and the copper dissolves as potassium cuprocyanide. When the current density is raised to 59 milliamp. per sq. cm. a dark grey oxide film sweeps up the metal and the *P.D.* between the electrodes rises from 1.6 to 2.7 volts. After a few seconds, the dark film gives place to a white film, presumably of cuprous cyanide, which travels down the metal, and the *P.D.* resumes its former value. The two states oscillate thereafter in regular periods.

In every respect this phenomenon is similar to the periodic electrolysis of chloride solutions, and the oxide film reacts towards interruption of the current just as in the former cases. It is therefore a logical deduction that the mechanism is precisely similar. The limits of the conditions favouring periodicity in the cyanide solutions are, however, very much narrower than in the chloride solutions. If a current density-potential curve similar to Graph 58 be constructed for a cyanide solution, the region of instability BFHD is very short and is indeed easily overshoot, the electrode often going straight from the state represented by B to that represented by H. It is only by increasing the current density cautiously that the intermediate oscillating condition can be realised in this system.

Another point differentiates the systems. On further increasing the current density to 86 milliamp. per sq. cm., a pale green film permanently covers the anode. At this stage, cuprous cyanide is being formed more quickly than it can dissolve in the potassium cyanide solution. The onset of this film is marked by a rise in

potential from 3.6 to 6.2 volts, after which a second series of oscillations ensues. These are most diverse in character, varying in amplitude from 0.1 to 6.0 volts and in wave-length from 0.1 to 5.0 seconds. Occasionally they become regular for some few minutes, after which the voltmeter needle behaves in an erratic manner, violent trembling being interspersed with sudden momentary darts up to a high value. Current densities exceeding 140 milliamp. per sq. cm. are beyond the region of periodicity in the cyanide film, but the erratic behaviour may be repeated by again lowering the current density. Since no change can be observed in the film in this second series of oscillations, there are as yet no data to afford an explanation. Analogy would suggest that the cyanide is first deposited in an unstable form at the high current density employed.

The phenomena are even better marked in 20% potassium cyanide solution. Illustrations of periodicity in the oxide film and of regular periods in the cyanide film are shown in Graphs 54 and 53 (Fig. 2), respectively. All these experiments on cyanide solutions were conducted at 20° because of the high frequency, and the solutions as a rule were not stirred in order to avoid loss of hydrogen cyanide. Control experiments in stirred solutions gave similar results, except that somewhat higher current densities were required in every case.

#### *Electrolysis of Other Solutions.*

*Sulphuric Acid.*—Investigations were carried out at intervals of 10% over the concentration range 100—10%, and also at 5, 2, and 0.5% (expressed as % by volume of acid, *d* 1.84). With concentrations above 50%, very little current would pass, the *P.D.* rapidly rising to a high value. After a time, cupric sulphate could be seen as crystals on the anode. Electrolysis followed a normal course below 10%, and at intermediate concentrations the potential rose to a high value at a certain critical current density. This was followed by a partial fall in the 40, 30, and 20% systems, but in no case was a periodic effect produced. It is probable that the highly resistant film was in this case copper sulphate. In the more dilute solutions (below 10%), some loosely adherent cupric oxide was always formed at high current densities. The 40% system was examined over a temperature range of 20° to 75°. Between these limits the critical current density increased from 58 to 138 milliamp. per sq. cm., but periodic effects were not produced.

*Nitric Acid.*—The concentrations examined were 10, 5, 2, and 0.5% (by volume of acid of *d* 1.42). In all these cases, the electrolysis pursued a steady course over the whole range of current densities. At the end of each experiment, the anode was covered



with a slimy, black deposit, probably of cupric oxide, which did not increase the resistance of the system. In one experiment with 5% nitric acid, continuous oscillations with a 30-second period between 0.8 and 1.0 volt were observed, using a current density of 36 milliamp. per sq. cm. Subsequent attempts to repeat this have failed. It is possible that the periods were due to some accidental circumstance, or that their range of existence was very narrow.

*Sodium Hydroxide.*—Solutions of concentrations graded from 8% to 0.4% were used. With the 8% solution at current densities below 5 milliamp. per sq. cm. a resistant film of cupric oxide slowly formed on the anode, the *P.D.* rising from 1.2 to 2.3 volts, at which oxygen was evolved. The film disappeared on increasing the current further and a greenish-yellow substance could be observed going into solution. Periods were not observed in any of these systems or in concentrated solutions of ammonia. A large number of mixtures of solutions of caustic soda and ammonia were also tried without success.

*Miscellaneous.*—Solutions of the following compositions were electrolysed with a copper anode over the range of current densities possible with the apparatus described and no trace of periodicity was observed. Ammonium acetate, 5 and 2.5%; sodium acetate, 8.4%; acetic acid, 12.4%; ammonium sulphate, 5, 2.5, and 1.25%; sodium nitrate, 5%; sodium hydrogen sulphite, 5 and 1%; potassium iodide, 5 and 1%; potassium chromate, 5 and 1%. With the last two substances, insoluble films immediately formed over the anode.

## (2) *Silver Anode.*

Although general considerations would lead one to anticipate that periodic phenomena might be observed at a silver anode in similar circumstances, the practical application is beset with difficulty in consequence of the insolubility of so many silver salts. Only the cyanide experiments can be repeated under precisely analogous conditions, but the insolubility of silver chloride has been overcome by the employment of ammoniacal solutions of chlorides. With these modifications, the phenomena observed are similar to the experiments with a copper anode, but, in general, the effects are much less striking; the amplitude of the oscillations is relatively small and the frequency is in all cases very high. The latter fact precludes direct experiment on the properties of the films, and it is therefore necessary at present to rely on the analogy with copper for an explanation of the phenomena. This seems a safe course in view of the similarity in every respect between the two cases.

*Electrolysis of Potassium Cyanide.*—Since, except in the strongest

solutions employed, the highest amount of current passing is small, the limits will be defined by the *P.D.* between the electrodes. With a 5% solution, the anode dissolves normally as potassium argentocyanide when the *P.D.* is less than 2.3 volts; at this value, a brownish-black film of silver oxide sweeps up the metal and the potential rises to 3.2 volts and then oscillates rapidly (about twice per second) between 3.2 and 3.0. Simultaneously, the upper part of the anode displays alternate black and white flashes—a rapid periodic dissolution of the silver oxide film by the potassium cyanide. The phenomenon is precisely similar to the case of copper, the black oxide film sweeping up and the white cyanide film rolling down, the frequency increasing with current density, concentration, and temperature. On slightly increasing the current, the alternation is so quick as to resemble a twinkling.

Similar effects were observed in solutions of concentrations 2.5, 1, 0.5, and 0.25%. The 2.5% solution gave an amplitude of 0.4 volt between the critical limits 1.7 and 2.9 volts. Below the value 1.7, no oxide film appeared and above 2.9 it existed permanently. The 1% solution gave an amplitude of 0.4 volt between the limits 1.8 and 2.7 volts. The limiting voltages for the 0.5% solution were 1.8 and 2.4, and in the case of the 0.25% solution they were 1.6 and 1.7. In the last case, the periods were as long as 30 seconds. It is seen from these figures that the extent of the unstable region decreases with progressive dilution.

These results were for unstirred solutions at 20°. In stirred solutions, the frequency was even higher. Since the low amplitude and high frequency of these periods were reminiscent of the anodic dissolution of copper in hydrochloric acid at higher temperatures, some experiments were conducted on silver in potassium cyanide solutions at 0°, and a maximum amplitude of 2.1 volts was then obtained with a 10% solution of potassium cyanide.

Experiments were also conducted in 10 and 5% ammonium thiocyanate solutions. Although above a certain current density the oxide film formed slowly, it seemed to be permanent. The 10% solution was investigated over the temperature range 20–80° in an attempt to quicken the dissolution of the film, but the experiments were not successful in producing periods.

*Electrolysis of Ammoniacal Solutions.*—When solutions of ammonium chloride were electrolysed with a silver anode, a highly resistant chloride film immediately formed. Attempts were therefore made to add just sufficient ammonia to dissolve the film as fast as it formed. Periodic effects were observed in these experiments, the anode becoming intermittently coated by a dark brown oxide film. The best result was with a solution of 50 c.c. of 10% ammonium

chloride and 50 c.c. of ammonia solution ( $d$  0.880). With a current density of 44 milliamp. per sq. cm., the *P.D.* oscillated between 3.0 and 4.1 in periods of 20 seconds. Rapid oscillations were also observed with a silver anode dissolving in a mixture of 50 c.c. of 10% ammonium sulphate solution and 50 c.c. of ammonia ( $d$  0.880).

Electrolysis of strong ammonia solutions alone might be anticipated to yield periodic phenomena on the basis of the explanation advanced here. Such solutions were tried without success, but the failure is most likely due to the fact that very little current can be made to pass. Endeavours to obviate this difficulty by adding progressively increasing amounts of caustic soda to the solution met with no success.

*Electrolysis of Sulphuric Acid.*—Solutions varying in composition from 100 to 2% were electrolysed. The anode dissolved continuously only in the most concentrated solutions, a sulphate film forming above a certain critical current density and the potential rising very sluggishly. Periods were obtained in these systems at higher temperatures. With 90% sulphuric acid at 50°, the waves shown in Graph 55 (Fig. 2) were obtained at a current density of 36 milliamp. per sq. cm., whilst Graph 56 represents 50% sulphuric acid at 75° under a current density of 17 milliamp. per sq. cm. The solutions always became cloudy, preventing observation of the state of the anode.

*Electrolysis of Other Solutions.*—In addition to those mentioned above, the following solutions gave no periodic effects: caustic soda, 8, 4, and 0.4%; nitric acid, 2, 1, and 0.5%; silver nitrate, 1.7%; acetic acid, 12.4%; potassium chromate, 9.7, 4.8, 2.4, and 0.6%; sodium thiosulphate, 3.4%; sodium hydrogen sulphite, 5%. In the last two cases, where periodicity might have been expected, the reaction followed a complex course, the main product being silver sulphide, whilst the solution developed the smell of hydrogen sulphide.

The investigation is being extended to anodes of other metals and will include the cathodic deposition of metals.

### *Summary.*

Periodic changes in current strength and in the *P.D.* between the electrodes were observed in the anodic dissolution of copper in solutions of hydrochloric acid, ammonium chloride, sodium chloride, cupric chloride, and potassium cyanide, and of silver in solutions of potassium cyanide, sulphuric acid, and ammoniacal ammonium sulphate and ammonium chloride. In every case, periodic film formation over the anode occurred. The case of copper in hydrochloric acid was the subject of a detailed examination. The pheno-

menon took place between certain limiting values of current density and the critical current density required to produce the periods was a linear function of the concentration of the electrolyte. The frequency of the periods increased with rising temperature and concentration, and decreased with rising current density. The periods were not affected by catalytic poisons. At the critical current density, an oxidic film formed over the metal and it was shown that this film was stable above a certain value of the current density; its metastability between this value and the critical current density is believed to be the cause of the phenomenon. This case appears to be typical of all the others investigated.

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### CXCIX.—*The Existence of the Suboxides of Lead and Thallium.*

By FREDERICK AUFENAST and HENRY TERREY.

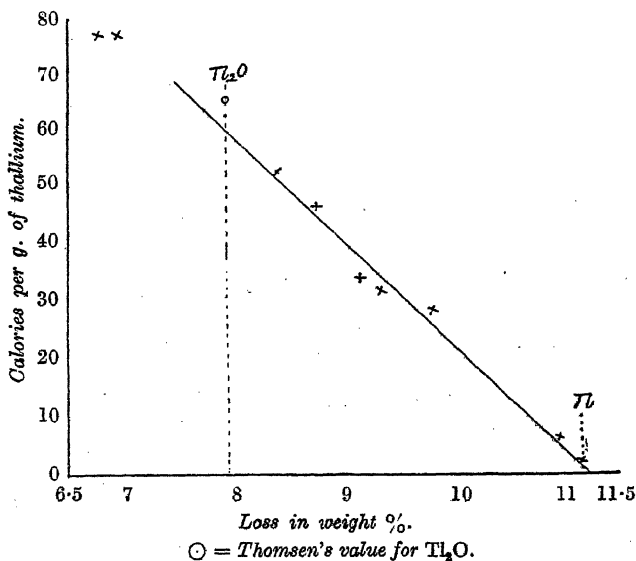
THE black substance obtained by heating lead oxalate has been interpreted as (1) a mixture of litharge and lead, or (2) lead suboxide. The work of Tanatar (*Z. anorg. Chem.*, 1901, 27, 304) on its heat of reaction with acetic acid pointed to a chemical entity, since he obtained results which indicated a heat of decomposition of lead suboxide into lead and litharge,  $\text{Pb}_2\text{O} \rightarrow \text{Pb} + \text{PbO} - 5,450$  cals. This view is supported by the work of Brislee (*J.*, 1908, 93, 154) and of Denham (*J.*, 1917, 111, 29; 1918, 113, 249; 1919, 115, 109). Evidence has also been given for the existence of subvalent lead ions by Denham (*J.*, 1908, 93, 41), Denham and Allmand (*ibid.*, p. 833), and Bell (*Trans. Faraday Soc.*, 1915, 11, 74).

The similarity of thallium and lead and of many of their salts suggests the possible existence of a thallium suboxide (compare Crookes, *Proc. Roy. Soc.*, 1862, 12, 150; Lorenz, *Z. anorg. Chem.*, 1896, 12, 439).

Investigations were first carried out to determine whether breaks could be obtained in the reduction-velocity curves such as were found by Brislee (*loc. cit.*). Thallous oxide was reduced in a stream of hydrogen and the amount of reduction was measured at regular intervals. The results showed in some cases a slight break in the curve corresponding to a compound  $\text{Tl}_4\text{O}$ , but these breaks were

not definite enough to be regarded as satisfactory evidence. Experiments were then made on the heat of solution of the products of varying composition obtained by reduction of thallic oxide, and the results are shown in Fig. 1, in which heats of solution per g. of thallium are plotted as ordinates and the extent to which the thallic oxide had lost weight on reduction as abscissæ. If a suboxide had been present, the heat of solution in 3*N*-sulphuric acid would have included a heat of decomposition of the suboxide and the graph would not have been a straight line. Within the limits of experimental error, no evidence was thus obtained for the existence

FIG. 1.



of thallium suboxide. Attempts were also made to measure the oxidation velocity of metallic thallium, but they were abandoned when it was found that the finely-divided metal was never oxidised completely although the initial velocity was very great.

Similar calorimetric experiments, in which the products of decomposition of lead oxalate were dissolved in acetic acid, gave results indicating that this supposed suboxide was a mixture of litharge and lead.

#### EXPERIMENTAL.

For the reduction velocity experiments, thallic oxide was precipitated from a thallic chloride solution by ammonia, washed, and heated to 200° in a current of oxygen to remove the last traces

of water. As thalious oxide is very deliquescent, it was decided to measure the reduction by collecting the water evolved rather than by removing the substance and determining the loss in weight. A weighed amount of thallic oxide, spread in a thin layer in a porcelain boat, was gradually heated electrically to  $150^{\circ}$  in a stream of hydrogen. After a few hours, when scarcely any more water was given off, the temperature was raised to  $185^{\circ} \pm 1^{\circ}$  and the water produced was collected in calcium chloride tubes which were weighed hourly. The complete reduction to thalious oxide, which took about 30–40 hours, was thus spread over a few days. The product was at first black, changing to a metallic grey colour.

For the heat of solution experiments a known weight of thallic oxide was reduced in a stream of hydrogen to a known composition, and the product was transferred as quickly as possible to the calorimeter, which consisted of a 100 c.c. Dewar vessel fitted with a Beckmann thermometer and a small glass stirrer and containing 25 c.c. of 3*N*-sulphuric acid. The results of these experiments are as follows :

Expt.	Wt. $\text{Tl}_2\text{O}_3$ used.	Loss %.	Wt. used for solution.	Rise in temp.	Cals. evolved.	Cals. per g. $\text{Tl}$ .
1	0.3926	6.78	0.3657	0.780°	26.86	77.29
2	0.4081	6.96	0.3797	0.809	27.86	77.21
3	0.3669	8.75	0.3242	0.404	13.91	47.36
4	0.4781	8.39	0.4257	0.693	21.44	53.30
5	0.4115	9.14	0.3655	0.400	12.38	34.73
6	0.3494	10.96	0.3029	0.067	2.07	6.81
7	0.3953	11.15	0.3394	0.025	0.77	2.28
8	0.3836	9.33	0.3151	0.325	10.06	32.66
9	0.3693	9.80	0.2848	0.266	8.20	29.51

For Expts. 1–3 and 4–9, the water-equivalent of the calorimeter and its contents was 34.43 g. and 30.94 g. respectively.

These results are shown graphically in Fig. 1, where the figures of column 3 are the abscissæ and those of column 7 the ordinates.

For the preparation of lead suboxide, about 1.5 g. of lead oxalate were heated in a porcelain boat in a vacuum at about  $275^{\circ}$ ; the gas evolved was pumped off periodically, the pressure never being allowed to exceed 1 cm. Evolution of gas ceased after about 24 hours, and the black residue gave off no carbon dioxide when treated with acids. The heat of solution in *N*-acetic acid was determined as with thallium, and after completion of the determination the liquid was filtered from undissolved lead, and the lead in the filtrate and the insoluble lead were determined by conversion into sulphate.

The results of two such experiments are given :

(Water-equivalent of calorimeter and contents = 56.2 g.)

	No. 1.	No. 2.
Weight of suboxide used (g.) .....	1.332	1.162
Amount of PbO dissolved from suboxide (%) ...	71.3	68.6
Rise in temperature .....	1.165°	0.963°
Heat of solution per g.-mol. of PbO (cals.) .....	15,370	15,140

The mean of these two experiments, *viz.*, 15,250 cals., differs only by about 350 cals. from that obtained with pure litharge, *viz.*, 15,600 cals.

These values are in agreement with those obtained by Sveda (*Chem. Listy*, 1923, 17, 47, 81, 112), but differ from those of Hersch-kowitsch (*Z. anorg. Chem.*, 1921, 115, 159) and Tanatar (*loc. cit.*).

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### CC.—*The Precipitation of Cadmium Sulphide from Aqueous Solutions of Cadmium Chloride in the Presence of Hydrochloric Acid and Other Chlorides.*

By SUBRAMONIA KRISHNAMURTI.

THE object of this investigation was to determine the relation between the concentration of cadmium chloride and the minimum concentration of hydrochloric acid required to prevent the precipitation of cadmium sulphide by hydrogen sulphide at constant temperature and pressure, and to ascertain the effect of various chlorides on this relation. It will be seen that the introduction of the activity concept renders this familiar problem of analytical practice capable of much more exact theoretical treatment. The present paper forms an introduction to the study of this and allied reactions from this point of view. Amongst previous workers on the precipitation of sulphides, mention may be made of Bruner and Zawadski (*Bull. Acad. Sci. Cracow*, 1909, 267; *Z. anorg. Chem.*, 1910, 67, 454), who studied more especially the precipitation of thallos sulphide, and of Baubigny (*Compt. rend.*, 1888, 107, 1148), who investigated the concentration of free acid required to prevent the precipitation of zinc sulphide from solutions of zinc sulphate. Reference may also be made to the work of Bruni and Padoa (*Atti R. Accad. Lincei*, 1905, 14, ii, 525) and of Glixelli (*Z. anorg. Chem.*, 1907, 55, 297).

#### EXPERIMENTAL.

The apparatus used was very simple. A stream of washed and pre-heated hydrogen sulphide was bubbled through the solution contained in a suitable vessel, placed in a thermostat at 25°. The

gas escaped through an oil-trap. In order to prevent the oxidation of hydrogen sulphide, air-free water was used in making up all solutions, whilst a stream of carbon dioxide was passed through the apparatus and solution for a considerable time before the hydrogen sulphide was admitted. A pre-saturator (also in the thermostat) contained hydrochloric acid of the same concentration as that contained in the precipitation vessel. In order to obtain reproducible results, in addition to the above precautions the precipitation vessel must be cleaned very thoroughly before use. The experiments were carried out by making up a series of solutions having the same concentration of cadmium chloride and gradually increasing concentrations of hydrochloric acid. In this way, two neighbouring solutions were obtained, in one of which a precipitate just appeared whilst in the other it did not. These two solutions were then made the limiting members of a new series in which the acid concentrations were graded more closely than before, and the interval between precipitation and non-precipitation was thus more accurately determined. Proceeding in this way, it was found possible to distinguish between two solutions differing by not more than 0.1*N*. The mean of these two hydrochloric acid concentrations was taken as giving the "critical" concentration for the given solution of cadmium chloride (expressed as mols. per litre), and the results are in the first two columns of Table I.

A second series of experiments was made with solutions in which the chloride of potassium, sodium, lithium, barium, or calcium was added so as to be present in *N*-concentration. The results are in the last five columns of Table I, which show in each case the critical concentrations of hydrochloric acid corresponding to each concentration of cadmium chloride.

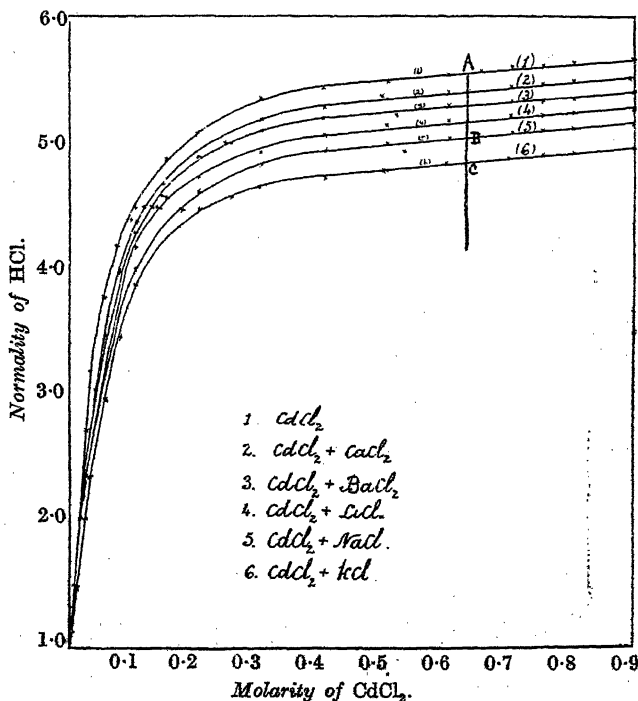
TABLE I.  
Limiting concentrations of HCl in the presence of

$\text{CdCl}_2$	—	<i>N</i> -KCl	<i>N</i> -NaCl	<i>N</i> -LiCl	<i>N</i> -BaCl <sub>2</sub>	<i>N</i> -CaCl <sub>2</sub>
0.005	1.50	1.20	1.30	1.35	1.40	1.40
0.01	2.05	1.50	1.60	1.65	1.75	1.80
0.03	3.20	2.40	2.50	2.55	2.60	2.65
0.05	3.80	3.00	3.15	3.25	3.35	3.50
0.08	—	3.50	3.60	3.75	4.10	4.15
0.10	4.50	3.90	4.00	4.20	4.30	4.40
0.20	5.20	4.50	4.60	4.70	4.90	5.00
0.30	5.40	4.60	4.85	4.95	5.10	5.20
0.40	5.45	4.75	4.95	5.05	5.20	5.30
0.50	5.55	4.80	5.00	5.15	5.25	5.35
0.60	5.60	4.85	5.05	5.20	5.30	5.40
0.70	5.65	4.90	5.10	5.25	5.35	5.45
0.80	5.70	4.95	5.10	5.25	5.35	5.50
0.90	5.75	4.95	5.15	5.30	5.40	5.55
1.00	5.75	5.00	5.20	5.30	5.40	5.60



The results contained in Table I are shown in Fig. 1. It will be seen that the critical concentration of hydrochloric acid increases very rapidly with increase of cadmium chloride concentration for the lower concentrations, whilst for the higher concentrations the variation of the hydrochloric acid concentration is comparatively small. It will also be seen that the effect of the neutral chlorides is to lower the critical concentration of hydrochloric acid corresponding to any given concentration of cadmium chloride, which

FIG. 1.

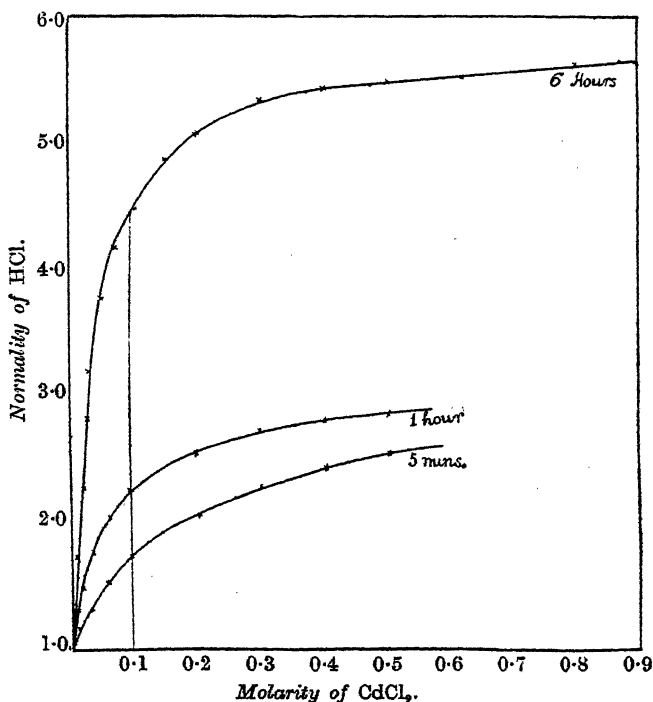


means that in the presence of these chlorides a lower concentration of hydrochloric acid suffices to prevent precipitation of cadmium sulphide, thus pointing to an activation of the acid by the neutral chloride.

*The Time Factor.*—A surprising feature of these results is the relatively high concentrations of hydrochloric acid required just to prevent precipitation. This critical concentration increases rapidly with time. Passing in hydrogen sulphide for 5 minutes and for 1 hour, respectively, gave the results shown in the two lower curves of Fig. 2. On increasing the duration of passage of the gas, the

critical concentration of hydrochloric acid steadily rose, reaching a limit after about 6 hours (see highest curve), *i.e.*, further passage of the gas produced no measurable variation in the required concentration of acid. Glxelli (*loc. cit.*) noticed a similar "period of induction" in his experiments on the precipitation of zinc sulphide. The experimental results given in Table I correspond in all cases to a duration of 6 hours for the passage of hydrogen sulphide. The

FIG. 2.



influence of this apparent supersaturation effect is shown in Table II, which gives, for a 0.1*M*-solution of cadmium chloride at 25°, the critical concentrations of hydrochloric acid corresponding to different lengths of time.

TABLE II.

Mols. HCl per litre .....	1.7	2.3	4.5
Time (min.) .....	5	60	300

*E.M.F. Measurements.*—If we apply the simple laws of chemical equilibrium to the ionic reactions occurring in such a precipitation of sulphide, then, for the points on the "precipitation curve"

(i.e., the curve separating the region of precipitation from that of non-precipitation), we have the two equations

$$[\text{Cd}^{++}] \cdot [\text{S}^{--}] = \text{const.}$$

$$[\text{H}^+]^2 \cdot [\text{S}^{--}] = K[\text{H}_2\text{S}].$$

The first equation involves, of course, the doubtful assumption that the points on the precipitation curve correspond to equilibrium with a definite crystalline cadmium sulphide present in not too fine a state of division. If we assume further that the solubility of the hydrogen sulphide and also its dissociation constant do not appreciably change with the total electrolyte content of the solution, then the right-hand member of the second equation remains constant, and division of the equations gives  $[\text{Cd}^{++}]/[\text{H}^+]^2 = \text{const.}$ , an equation which is often used in elementary treatises on the theory of inorganic analysis. For very dilute solutions, we may use the approximate form  $[\text{CdCl}_2]/[\text{HCl}]^2 = \text{const.}$  If we apply this equation to the results given in columns 1 and 2 of Table I for the dilute solutions of cadmium chloride (although the corresponding concentrations of hydrochloric acid are by no means dilute), we obtain the results shown in Table III: the quotient rises slowly.

TABLE III.

$[\text{CdCl}_2]$ .....	0.005	0.01	0.02	0.03	0.05	0.10
$[\text{HCl}]$ .....	1.50	2.05	2.75	3.20	3.80	4.50
$10^4 \times [\text{CdCl}_2]/[\text{HCl}]^2$ ...	22	25	26	29	34	49

Rewriting the former equations in terms of activities, we have

$$a_{\text{Cd}} \cdot a_{\text{S}} = L$$

$$a_{\text{H}}^2 \cdot a_{\text{S}} = K_1 a_{\text{H}_2\text{S}}$$

where  $L$  is the activity of the solid sulphide and  $K_1$  the "thermodynamic" dissociation constant of hydrogen sulphide. Since the temperature and the pressure of hydrogen sulphide in the gas phase are constant,  $a_{\text{H}_2\text{S}}$  is now strictly constant. We may also regard  $K_1$  as a constant, hence for points on the precipitation curve

$$a_{\text{H}}^2/a_{\text{Cd}} = K_1 a_{\text{H}_2\text{S}}/L = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation will be much more exact than the former one, although it still involves the assumption that we are dealing, along the precipitation curve, with a definite "solid" cadmium sulphide of not too small a grain size, or, at all events, of constant grain size in the different experiments. It is possible to test equation (1) by measuring the *E.M.F.* of cells of the type  $\text{Cd amalgam} | \text{CdCl}_2 + \text{HCl} | \text{H}_2 \text{ gas at constant pressure}$ . A dilute cadmium amalgam of definite concentration is used instead of solid metallic cadmium, in order to

avoid irreversible evolution of hydrogen at the cadmium electrode. The *E.M.F.* of the cell is given by the equation

$$E = E_0 + RT/2F \cdot \log a_{H^2}/a_{Cd} \quad (2)$$

Hence, if we employ in the cell solutions corresponding in composition and concentration to points on the precipitation curve, *E* will be constant if equation (1) holds good for such points, since we may neglect the effect of the dissolved hydrogen sulphide. Cells of this sort were set up, with hydrogen electrodes of the usual type, and yielded constant and reproducible results after an hour. The results are in Table IV (to the nearest millivolt).

TABLE IV.

CdCl <sub>2</sub> (mol./litre)	0.005	0.01	0.02	0.05	0.08	0.10	0.20	0.30	0.50
HCl (mols./litre)	1.50	2.05	2.75	3.80	4.20	4.50	5.20	5.40	5.55
<i>E.M.F.</i> (millivolts)	481	481	481	481	482	481	482	482	480

The constancy in the *E.M.F.* indicates that the points on the observed precipitation curve do correspond to definite equilibria, and supports the view that this curve is a true border curve separating the region of precipitation from that of solution (non-precipitation).

*Neutral Salt Effect.*—The curves numbered (2) to (6) in Fig. 1 show the changes in the precipitation curve caused by the presence (in *N*-concentration) of a series of neutral chlorides. The interpretation of these neutral salt effects from the point of view of ionic activities can be seen from a consideration of the figure. At the point A on the precipitation curve of cadmium chloride (*i.e.*, without addition of any neutral chloride) we have the relation

$$a_{H^2}/a_{Cd} = K_1 a_{H_2S}/L.$$

Suppose now that the solution corresponding to point A is made *N* with respect to, *e.g.*, potassium chloride, everything else remaining the same. Since A lies above C, it is clear that A now falls in the non-precipitation region, and hence  $a_{Cd} \cdot a_S < L$ . In the mixed solution corresponding to point A, therefore,  $a_{H^2}/a_{Cd} > K_1 a_{H_2S}/L$ . The effect of the addition of potassium chloride has thus been to increase the value of the quotient  $a_{H^2}/a_{Cd}$  and this value can be brought back to the original value,  $K_1 a_{H_2S}/L$ , only by reducing the concentration of hydrochloric acid to the value corresponding to point C. Now it is well known that the addition of chlorides can increase the value of  $a_{H^+}$  in a solution of hydrochloric acid (Poma, *Z. physikal. Chem.*, 1914, 88, 671; Harned, *J. Amer. Chem. Soc.*, 1915, 37, 2460; Fales and Nelson, *ibid.*, 1915, 37, 2769; Thomas and Baldwin, *ibid.*, 1919, 41, 1981). In the present case, this action will produce

a very marked result, owing to the occurrence of  $a_{H^+}^2$  in the numerator of the quotient. It is probable that owing to complex anion formation and other causes the addition of chlorine ions (from the neutral chlorides) will *decrease* the value of  $a_{Cd}$  occurring in the denominator. We have therefore good reasons for concluding that the addition of a neutral chloride will increase the value of  $a_{H^+}^2/a_{Cd}$ .

If we ascribe the chief effect to the increase in the value of  $a_{H^+}$ , we should expect from the results of the investigations previously quoted that the effect would decrease in the order  $LiCl > NaCl > KCl$ , whereas the results in Table I would appear to give the order  $KCl > NaCl > LiCl$ .

Further discussion of this matter would not be profitable without more detailed and extensive data.

#### *Summary.*

1. The concentrations of hydrochloric acid which are just sufficient to prevent precipitation of solutions of cadmium chloride by hydrogen sulphide at  $25^\circ$  and atmospheric pressure have been determined.

2. The effects produced on these critical concentrations of hydrochloric acid by a number of neutral chlorides in *N*-concentration have been determined.

3. The cadmium chloride-hydrochloric acid "precipitation" curve has been considered from the point of view of ionic activity, and predictions based thereon have been confirmed by *E.M.F.* measurements.

4. The effects produced by the addition of neutral chlorides have been considered in the light of previous work on the influence of such salts on the hydrogen-ion activity.

5. The precipitation experiments reveal a "supersaturation" or "induction" delay in the appearance of the precipitate, an effect previously noted by Glaxelli in the precipitation of zinc sulphide.

It is intended to extend this investigation and to include allied cases.

The work described was carried out at the suggestion and under the direction of Professor F. G. Donnan, to whom the author desires to express his thanks for advice and assistance.

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*CCI.—The Interaction of Hydrogen and Nitrous Oxide on the Surface of Gold.*

By WILLIAM KENNETH HUTCHISON and CYRIL NORMAN HINSHELWOOD.

IN catalytic reactions at surfaces considerable variety is found in the relations which exist between the rate of reaction and the concentrations of the several reacting substances. Examples of different kinds have been given in a number of previous papers. The most general relation, when there is one reacting substance only, is that the rate increases with concentration according to a curve of the same form as an adsorption isotherm. When there are two reacting substances, the rate may actually pass through a maximum and decrease again as the pressure of one gas increases, the decrease being due to the displacement of the other gas from the surface. But it may happen that the two reacting substances are independently adsorbed on different active parts of the surface. Saturation can then be reached with respect to each gas without displacement of the other. Examples of these two kinds of behaviour are given in J., 1925, 127, 806, 1546. For the sake of completeness in classifying the various types of heterogeneous reaction, further instances may be useful.

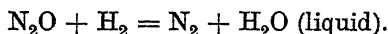
We have now investigated the kinetics of the interaction of hydrogen and nitrous oxide on the surface of a gold wire. The results can be interpreted by assuming that hydrogen and nitrous oxide are adsorbed on the surface independently of each other, and that interaction can take place between adjacent molecules. The reaction rate increases with increase in the pressure of nitrous oxide, and reaches a limiting value at approximately 300 mm., after which it remains constant up to the highest pressure used, *viz.*, 500 mm. The absence of any fall in the rate at the higher pressures may be taken to show that, even after saturation is reached, there is no appreciable tendency for the nitrous oxide to displace the hydrogen from the surface.

Increase of hydrogen pressure has a similar effect, except that the limiting value of the rate is not quite reached within the experimental limit of 500 mm.

A second effect was traced to the hydrogen, namely a steady decrease in the activity of the wire, especially when it was heated in mixtures containing hydrogen in excess. On a wire, the activity of which had been reduced in this way to less than one-fifth of its initial value, it was found that the influence of the nitrous oxide on the rate was more nearly proportional to its pressure, and that the

limiting or saturation value could not be reached. It is suggested that hydrogen gradually dissolves in the body of the metal—this solution being distinct from its primary adsorption on the surface—and decreases the adsorptive power towards nitrous oxide. This would result, not only in a decrease in the rate of reaction due to the smaller number of nitrous oxide molecules present on the surface, but also in a change in the actual adsorption isotherm.

The method of procedure was that already described (*loc. cit.*), the change in pressure giving a measure of the reaction



A correction was necessary for the vapour pressure of liquid water at 0° in those cases where no drying agent was present. The experimental work was complicated by the continually decreasing activity of the catalyst. Heating to dull redness in air caused a partial but only temporary recovery, for it rendered the wire very susceptible to the further action of hydrogen. The following method was therefore employed to correct for the variable activity, and to reduce the results to values which are comparable with one another. Initial rates of reaction only were observed, and in any series, the first, third, and odd-numbered experiments were performed under standard conditions of concentration of the reactants (for convenience, 100 mm. of each), and in the even-numbered experiments the initial pressure of one or other reactant was varied. The ratio of the observed initial rate in an even-numbered experiment to the mean value of the rates observed in the reference experiments on either side of it gives a value which is strictly comparable with the others in a given series, even if the state of activity of the catalyst drifts to some extent.

Owing to this gradual poisoning of the catalyst, and also on account of the complicated relation which would be required to express the velocity in terms of the concentration of both reactants, no attempt was made to evaluate velocity coefficients, nor to determine the heat of activation. The experiments were carried out in the usual manner at two temperatures with a number of different wires, and in the tables which follow it will be seen how the initial rate of reaction depends upon the initial pressure of nitrous oxide and of hydrogen. If, as seems probable, the rate is determined by the amount of adsorption or surface concentration, these figures represent also the relative degrees of saturation of the active parts of the surface with the gas in question.

*Influence of Nitrous Oxide.*—On a fresh active wire the initial rate reaches a limit at a pressure near 300 mm. and remains constant up to a pressure of at least 500 mm.

TABLE I.

Pressure of hydrogen = 100 mm.

	Pressure of N <sub>2</sub> O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1.00	1.40	1.64	1.91	1.80	Wire 1	704°
" " ...	1.00	1.18	1.34	1.37	1.38	Wire 2	
" " ...	1.00	—	1.25	—	1.26	Wire 3	
" " ...	1.00	—	1.77	—	1.89	"	880°

With a wire in a highly poisoned and inactive state, as a result of the prolonged action of hydrogen, saturation was not reached, and the rate varied considerably more extensively with the initial pressure of nitrous oxide.

TABLE II.

Pressure of hydrogen = 100 mm. (Wire poisoned.)

	Pressure of N <sub>2</sub> O (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1.00	1.50	2.10	2.50	—	Wire 2	704°
" " ...	1.00	1.76	2.56	3.13	3.68	"	880°

*Influence of Hydrogen.*—The influence of the pressure of hydrogen on the rate appears to be independent of the state of the wire, as the figures of Table III show. Saturation is not reached so readily as in the case of nitrous oxide.

TABLE III.

Pressure of nitrous oxide = 100 mm.

	Pressure of H <sub>2</sub> (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1.00	1.33	1.58	1.97	2.22	Wire 4	704°
" " ...	1.00	1.21	1.50	1.78	1.92		
" " ...	1.00	1.18	1.43	1.40	1.81	Wire 2 (poisoned)	880°

*Influence of Water Vapour.*—Experiments were performed in which phosphoric oxide was present either in the bulb or in a small side tube sealed to it. The rate was reduced somewhat, as compared with that observed on the same wire before the introduction of the phosphoric oxide, and a certain recovery took place when the side tube containing it was sealed off, but the change was not fundamentally important. Further, a comparison of the results contained in Tables IV and V with those already discussed shows that the adsorption isotherms remain of the same form, whether water vapour is present or not.

This reaction possesses some interest in connexion with the general classification of heterogeneous reactions, as it represents



TABLE IV.

Pressure of hydrogen = 100 mm. (Fresh wire.)

	Pressure of $N_2O$ (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1.00	1.34	1.56	1.59	(1.31)	Wire 5	704°

TABLE V.

Pressure of nitrous oxide = 100 mm. (Fresh wire.)

	Pressure of $H_2$ (mm.).						
	100.	200.	300.	400.	500.		
Relative initial rate...	1.00	1.63	—	2.00	2.73	Wire 5	704°

one of the most general cases. But rather will it be in certain special circumstances, for example, with very small or very large adsorption of one reactant, that further theoretical inferences will become possible.

*Summary.*

The relation between the rate of interaction of nitrous oxide and hydrogen at the surface of a gold wire and the concentrations of the two gases has been examined at 704° and 880°. The reaction is of the type where the two gases are adsorbed independently of each other. The rate of reaction tends to a limiting value as the pressure of each gas is increased.

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[Received, May 17th, 1926.]

CCII.—*The Specific Heats of Hydrogen Cyanide. A Reply.*

By JAMES RIDDICK PARTINGTON.

A RECENT statement [(Mrs.) Ingold, this vol., p. 26] that there is no "obvious disagreement between the author's results and those of Partington and Carroll" for the ratio of the specific heats of hydrogen cyanide seems to call for correction. Whereas the value found by the last two experimenters at 20° was 1.282 (422 mm.), that of Mrs. Ingold at the lowest temperature used, 65°, was 1.310 (1 atm.), and the curve in Fig. 2 in Mrs. Ingold's former paper (J., 1922, 121, 1610) would indicate that at 20° the value should be of the order of 1.315, which is 2.3% higher than the value found by Partington and Carroll (*Phil. Mag.*, 1925, 49, 665). It is not considered that such agreement is satisfactory.

Mrs. Ingold has discussed in a very general manner the statement that "although the vapour is associated, the association is small" (Partington and Carroll, *ibid.*, p. 680). Since the critical data were not known at the time, the latter authors contented themselves with an approximate calculation, but the statement that this was "unjustified" is not confirmed by an examination of the paper. Some caution is necessary in approximate calculations, but this must not be mistaken for doubt as to the approximate validity of the results found. In reality, as Mrs. Ingold points out, the calculation of the critical constants has been very satisfactorily confirmed by the experiments of Bredig and Teichmann (*Z. Elektrochem.*, 1925, 31, 449), which appeared later, and these authors have repeated our calculations of  $c_p/c_v$  from our own and Mrs. Ingold's experiments and have shown that they are very close to those obtained with the actual experimental data for the critical constants. The regular nature of the curve in Fig. 2 in Mrs. Ingold's first paper would therefore seem to be disturbed in the manner previously pointed out by Partington and Carroll.

It would seem possible to test the assumption of a small association of hydrogen cyanide vapour by a calculation of the density on the assumption that deviations from the gas laws alone, without association, are operative, and then comparing the results with the experimental values. The method used is one which, it is stated (Ingold, this vol., p. 26), has "proved conclusively that, despite its enhanced density, the degree of association of water vapour, if not zero, is at any rate so small that the most accurate available measurements fail to show it." The densities have been calculated from the ideal value by division by

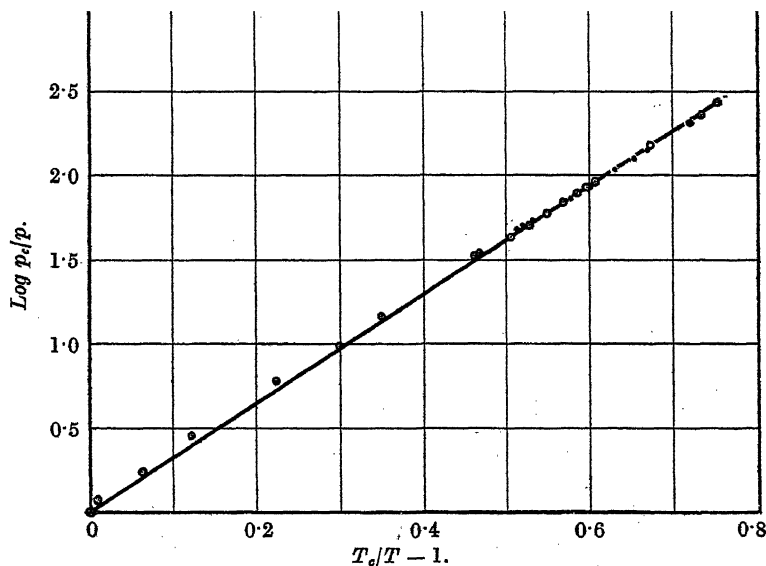
$$\lambda = 1 + \frac{9}{128}\pi\tau(1-6\tau^2)$$

in accordance with Berthelot's equation, which may be expected to apply with some accuracy at atmospheric pressure. In this expression,  $\pi$  and  $\tau$  have been calculated from the critical data of Bredig and Teichmann ( $p_c = 53.2$  atm.;  $T_c = 456.6^\circ$ ). The results in Table I indicate that, below  $100^\circ$ , the calculated densities are distinctly lower than those found by Mrs. Ingold. At  $65^\circ$ , the observed density, which lies on the smooth curve, is 2% higher than that corrected for deviations from the gas laws, although the experimental error is stated to be only 0.2%. (The two observed values at  $132^\circ$  and  $175^\circ$  lie well below the smooth curve.) This seems to indicate that, if the density measurements are as accurate as they are claimed to be, there must be some such small association of hydrogen cyanide vapour as was assumed by Partington and

Carroll, and that the opposite conclusion, arrived at by Mrs. Ingold on very general grounds, and without specific reference to hydrogen cyanide, is improbable.

In a cursory reference to Bredig and Teichmann's paper, Mrs. Ingold has not emphasised the fact that these authors show, by no fewer than five different sets of experimental data, that hydrogen cyanide is associated in the liquid state and that they express agreement with our calculations for the gas.

FIG. 1.



It is also of interest to plot the values of  $\log p/p_c$  against those of  $(T_c/T - 1)$ , in the manner used by van der Waals. Bredig and Teichmann refer to this in their paper, but do not reproduce the

TABLE I.

$t^\circ \text{C.}$	$T^\circ \text{abs.}$	$\tau.$	$\lambda.$	$\Delta \text{ obs.}$ (air=1).	$\Delta \text{ obs.}$ (O=16).	$\Delta \text{ calc.}$
65	338.1	1.3595	0.9822	0.968	14.06	13.77
96	369.1	1.2371	0.9866	0.951	13.79	13.70
97.5	370.6	1.2321	0.9868	0.952	13.80	13.70
132	405.1	1.1271	0.9901	0.936	13.57	13.66
140	413.1	1.1053	0.9907	0.938	13.60	13.65
175	448.1	1.0190	0.9930	0.932	13.51	13.61
177	450.1	1.0145	0.9931	0.934	13.54	13.61

curve. This curve has been constructed from the data of Bredig and Teichmann (*loc. cit.*) and of Perry and Porter (*J. Amer. Chem. Soc.*, 1926, 48, 299), the former being denoted by circles and the latter by dots on the curve. It will be seen from Fig. 1 that practi-

cally all the points lie on a straight line passing through the origin. The gradient of this line is 3.26. According to van der Waals the normal value is 3.0, whilst from the curve for water given by Nernst ("Theoretische Chemie," 8—10 Aufl., p. 248) the value 3.3 is found. It may be remarked that, in reality, the gradient depends somewhat on the molecular weight and that, although it is reasonable to compare water and hydrogen cyanide as associated substances, carbon disulphide, for which the gradient is lower than 3, should probably be chosen as a normal substance for comparison. There would seem to be very little, if any, doubt that hydrogen cyanide is associated in the liquid state.

#### *Summary.*

It is shown that the reasons advanced against the assumption of Partington and Carroll that hydrogen cyanide vapour is associated to a small extent at room temperature are inconclusive, and that when the qualitative arguments put forward on general grounds are applied quantitatively to the specific case of hydrogen cyanide they lead to conclusions exactly opposite to those arrived at by Mrs. Ingold. Attention is also drawn to the fact that all the experimental evidence, of various kinds, points to association in the liquid state.

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[Received, March 24th, 1926.]

### CCIII.—*The Laws of Aromatic Substitution. Part V.* *The Directing Effect of Electrolytically Dissociated Groups.\**

By BERNHARD FLÜRSCHHEIM and ERIC LEIGHTON HOLMES.

In previous communications of this series (*J. pr. Chem.*, 1902, 66, 321; 1905, 71, 497; 1907, 76, 165, 185) it was shown, *inter alia*, that the position in which a second substituent will enter a mono-substituted benzene ring (whether *op-*, or *m-*) can be unequivocally predicted from the affinity demand of the first substituent. In subsequent papers, a more general theory of reactivity was evolved, in which, beside the *affinity demand* (the "quantitative factor" = *q*), the *varying nature of the affinity of atoms* ("polar factor" = *p*) and their *steric effects* ("steric factor" = *s*) were taken into consideration. A review of the whole subject has recently been published in *Chemistry and Industry* (1925, 44, 246).

\* A brief preliminary communication of the ideas and the scope of the experiments contained in this paper is to be found in *Chem. and Ind.*, 1926, 45.

Whereas generally account must be taken of all three factors, there are cases, and even classes, of reactions where one or even two of them can be neglected. Thus the steric hindrance exercised by a first substituent in benzene affects substitution in the *o*-position, but its effect, and still more the difference of its effects, in the *m*- and *p*-positions are negligible. On the other hand, the polar effect of most substituents cannot be neglected in *any* position, but even here the *difference* of their influence on the *m*- and *p*-carbon atoms could be ignored in all the cases hitherto examined. This has been definitely established by numerous observations; thus, not even an accumulation of "negative" groups such as obtains in bromocyanophenylnitromethane,  $C_6H_5 \cdot CBr(CN) \cdot NO_2$ , can prevent the essentially exclusive *op*-substitution predicted from the affinity demand of the substituent (compare *J. pr. Chem.*, 1902, 66, 321).

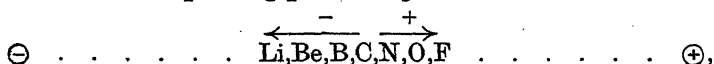
In view of this, an observation by Noeltling and Kregczy (*Bull. Soc. chim.*, 1916, 19, 355) seemed at first sight surprising. These authors nitrated diethylbenzylamine in sulphuric acid solution and obtained 35 to 40% of the *m*-nitro-derivative. Since the affinity demand of the substituent should lead to *op*-nitration only, this experiment has now been repeated, and through the use of very accurate methods of separation the yield of the *m*-nitro-compound has been found to be even higher, *viz.*, 44% of the isomerides formed.

This result could not be ascribed to nitration of the *free base*, since the hydrolysis of such a relatively strong base in an excess of strong sulphuric acid would be negligible. Neither could it be due to nitration of the *salt*, which should occur only in the *o*- and *p*-positions. Reference to the work of Walden and others having shown that salts possess a high degree of electrolytic dissociation in strong sulphuric acid, even at high concentrations, the question whether *m*-nitration of the *electrolytic ion* would be in accordance with the theory was next considered. Concerning the relative polar effects of different atoms, it had already been pointed out (*J.*, 1909, 95, 719) that an electric charge may be regarded as the most polar element. The meaning of this statement may be briefly explained.

Discarding all speculations concerning the origin and nature of chemical affinity, what we really *know* about it appears to be this: 1. Chemical affinity, like gravitational and magnetic forces, is *some* function of an atom. 2. Although atoms contain positive and negative electrical charges, there is no compelling reason for assuming that chemical force, any more than gravitational or magnetic force, is electrostatic. 3. The behaviour of atoms, not only towards electrical charges, but also *towards one another*, proves that chemical affinity varies in different atoms both in *amount* and in *kind*. The difference in kind is most pronounced between the

atoms of the elements situated at the opposite ends of a period in the periodic table and *gradually* diminishes with the number of intervening members of the period. The more two atoms differ as to the kind of their affinity, the greater is the difference in their tendencies to combine, either with a third atom located towards either end of a period, or with an electrical charge of a given sign.

We may conclude that the variation in kind exhibited by chemical affinity implies a *gradual transition in polarity*, involving a change of sign at a given point in a period. *This gradual transition, if extended far beyond the terminal members of a period, would lead to polarity in its extreme form—electropolarity.* In other words, *whilst electropolarity exists only in two extreme kinds of opposite sign, chemical polarity, gradually varying in kind, bridges a limited central region in the wide gap between the two electropolar extremes.* Thus, in view of the strong affinity of fluorine for an electron as well as for lithium, the corresponding period might be written :



polar attraction between two members of opposite sign, and polar repulsion \* between a given member and a more polar one of the same sign, running parallel with their distance apart within the period. This is what is meant by the polar factor *p* or “polar effect,” or, to use the term recently introduced by Lapworth, by “general polarity.”

The polar attraction by a negative charge, and the polar repulsion by a positive charge, of a halogen atom, nitro-group, etc., therefore considerably exceed the corresponding effects of an electrically neutral atom or group on these atoms or groups. Accordingly, since the polarity of such a charge is transmitted to different nuclear carbon atoms in different degrees ascertainable from the theory itself (J., 1910, 97, 85), a positive charge tends to direct an entering nitro-group, etc., to the least affected nuclear carbon atom, whereas a negative charge tends to direct it to the most affected carbon atom. In the benzoic anion and the diethylbenzylammonium kation, for instance, the nuclear atoms are affected in the order *o*->*p*->*m*- (on account of the direct neutralisation of residual affinity between the *p*-atoms which results in the *direct* transmission of the polar effect from the substituted atom to the *p*-atom) (see *loc. cit.*), so that the overpowering *p* of the electrical charge must favour substitution in the order *o*->*p*->*m*- in the benzoic anion and *m*->*p*->*o*- in the diethylbenzylammonium kation. Besides, it must have an acceler-

\* “Repulsion” is used in a relative sense only, to denote a reduced potential at corresponding points in the field of mutual attraction of the atoms. The affinity of neon, whilst much smaller in amount than that of fluorine, must be even more polar in kind.

ating effect in the anion and a retarding effect in the kation, as compared with the corresponding neutral compound.\*

This is exactly what has been found to occur. Electrolytically dissociated sodium benzoate is chlorinated by hypochlorous acid (Lossen, D.R.-P. 146, 174) with remarkable ease and in the order  $o \rightarrow p \rightarrow m$ -, whereas benzoic acid itself is brominated, by hypobromous acid, slowly and in the meta-position (Stark, *Ber.*, 1910, 43, 473). Electrolytically dissociated benzyldiethylammonium hydrogen sulphate is nitrated in the meta-position and more slowly than the undissociated salt, since  $m$ -substitution in an approximately normal solution amounts to 44% only, although the degree of dissociation of binary salts in strong sulphuric acid at a corresponding concentration is of the order of 80 or 90%.

The theoretical support thus afforded for the assumption that the observed *meta*-nitration is due to the electrolytic ion has been supplemented by direct experimental proof. The assumption requires that increased electrolytic dissociation should lead to increased *meta*-substitution, and *vice versa*. This has been found to be the case. At double the dilution, 52% of the  $m$ -nitro-derivative was formed, the increase being in approximate agreement with the value calculated from the increase in dissociation required by Sugden's cubic root law on the basis of *exclusive m*-nitration of the ion and *exclusive op*-nitration of the undissociated salt (see experimental part); any appreciable *op*-substitution in the ion and/or  $m$ -substitution in the salt would, according to Sugden's law and still more according to other dilution laws, have caused the increase in the amount of  $m$ -nitration to be correspondingly below the experimental result. Similarly, the introduction of a common ion by saturation of the nitrating solution with ammonium sulphate resulted in lowering the amount of *meta*-compound formed to 34%. In this case, only an approximate calculation is feasible, but it shows the decrease to be of the right order. If the dissociation of the sulphuric acid solvent itself (to which Dr. Sugden has kindly called the authors' attention) produced a common ion, then the change in  $m$ -nitration with varying concentration would be even greater than required by Sugden's law.

Complications such as have now been dealt with, where the uniquely strong  $p$  of an electrical charge conflicts with and outweighs  $q$ , can occur only where the charge is carried by an atom separated from the nucleus by *one* intervening atom. When the charged

\* This effect of the polar factor on the *velocity* of aromatic substitution has repeatedly been emphasised by one of the authors (*e.g.*, *Ber.*, 1906, 39, 2016; *J. pr. Chem.*, 1907, 76, 200), and its electronic equivalent recently by Robinson (this vol., p. 410) and co-workers.

atom is directly attached to the nucleus,  $p$  and  $q$  support each other. When the charged atom and the nucleus are separated by two or more atoms, the polar factor even of an electrical charge may be presumed to become negligible, at least as regards its effect on  $m$ - versus  $p$ -substitution.

The present results appear to supply a conclusive solution of the problem of  $m$ -nitration in solutions of benzylammonium salts and to be in complete agreement with the theory advanced by one of the authors. Apart from this they seem to show, for the first time, a way in which the changes of the "degree of dissociation" can be ascertained without interference from disturbing factors such as variations in viscosity, ionic mobility, and solvation. The results also furnish, perhaps not a final proof, but at least a strong argument against the theory of the complete dissociation of strong electrolytes and of the intramolecular ionisation of undissociated ammonium salts. On these views, the undissociated salt in solution would have to be replaced by its two ions in more or less close proximity. But in this case, the charge on the kation would be substantially nearer to the benzene ring than would the charge on the anion, and though it is perhaps not entirely impossible, it is at least highly improbable that the latter charge could seriously interfere with the transmission to the ring of the pronounced polar effect of the first charge. What appears quite certain, however, is that it could not do so in the case of Robinson's mechanism of transmission. Robinson, who has adopted the electronists' view that an ammonium group is ionised even in the undissociated salt (J., 1922, 121, 430), attributes *meta*-substitution to a "Lewis" electron shift towards the ammonium group caused by its positive charge (*Chem. and Ind.*, 1925, 44, 563; this vol., p. 410). But such a shift would occur both in the electrolytically dissociated and in the undissociated state, since in the latter the attraction of the electron by the positive charge would, according to Coulomb's law, be compensated by the repulsion of the more distant anionic charge only to a fractional extent (less than one-quarter). It would be less compensated than a positive charge on carbon in carboxyl, carbonyl, trichloromethyl, or on nitrogen in a nitro-group (since the acid radical is generally recognised to be at a greater distance from ammonium nitrogen than oxygen is from carbon or nitrogen, or than chlorine is from carbon), all these being cases where Robinson (*loc. cit.*) attributes *meta*-substitution to such a positive charge, thus obviously assuming it to be insufficiently compensated. Contrary to the experimental results, Robinson's theory would therefore require *meta*-substitution in the undissociated as well as in the dissociated portion, especially since his alternative (conjugation) cannot be applied in this case.



Neglect of the polar and steric factors in classes of reactions where—as has repeatedly been emphasised—they must not be neglected, has recently led several authors to erroneous objections, which will be dealt with in a subsequent communication.

#### EXPERIMENTAL.

Three series of nitrations of diethylbenzylamine were carried out. The first of these served to establish the best method of separating the isomerides formed. The second series (nitrations 1 to 5 in the table) gave the approximate results obtained by that method, whereas in the final series (nitrations 7 to 10) quantitative values were obtained by the determination of that portion of the *m*-nitro-compound which could not be separated as such.

The nitrations were carried out by Noelting and Kregczy's method (*loc. cit.*), but at  $-10^{\circ}$  to  $0^{\circ}$  instead of  $-5^{\circ}$  to  $+5^{\circ}$ . Nitric acid (Kahlbaum, "*d* 1.52") was used, except in No. 5, where ordinary fuming nitric acid served both as nitrating agent and as solvent. In Nos. 8 and 10, the nitrated mixture was kept at room temperature for  $1\frac{1}{2}$  hours, and 4 hours, respectively, instead of the usual 1 hour. To prevent any volatilisation of the nitro-bases formed, the benzene extract containing them was treated with picric acid before evaporation to dryness. The yield of crude nitro-bases was always close to 97.0% of the theoretical, and the picric acid added (2.60, 4.0, 6.71, 7.10, 2.60, 3.417, 6.48, 4.286, and 4.480 g., respectively, in nitrations 1 to 5 and 7 to 10) was either 97% of the theoretical or slightly more. The freezing-point method being untrustworthy in the presence of even small amounts of impurities, and fractional distillation of the free bases having failed, there only remained the following method, involving the use of an analytical balance throughout and weeks of work for each nitration of the final series:

The bulk of the relatively insoluble picrate of the *m*-isomeride was obtained pure by prolonged fractional recrystallisation from alcohol (see Noelting and Kregczy); this was preferably preceded by fractional extraction with small amounts of the solvent. This fractionation was carried especially far in Nos. 1, 8, and 10. In Nos. 2, 3, and 5, the pure picrate of the *p*-nitro-compound was also isolated, by further recrystallisation from glacial acetic acid, to the extent of 1.60, 2.30, and 1.09 g., respectively. The purity of the picrate of the *m*-nitro-compound was established by its correct and constant melting point, by the melting point of a mixture with a sample prepared from *m*-nitrobenzyl chloride and diethylamine, and by its oxidation to *m*-nitrobenzoic acid. The purity of the picrate of the *p*-compound, where isolated, was established by its correct

and constant melting point, and by the melting point of a mixture with synthetic material. The pure picrate, m. p.  $122^{\circ}$ , of the *o*-nitro-compound could only be obtained synthetically (Noelting and Kregczy give  $117^{\circ}$ ). The *picrate* of diethylbenzylamine itself crystallises in stout, yellow prisms, m. p.  $120^{\circ}$ . In the final series, the picrate of the *m*-nitro-compound left behind in the *op*-mixture was thus determined : 1 part of the picrate mixture was boiled under reflux with 120 parts of water and 2 parts of potassium permanganate. At intervals of 30 minutes three further additions of 2 parts of permanganate were made, then another after 40 minutes, whereafter boiling was continued for 3 hours. After the excess of permanganate had been destroyed by alcohol, the nitrobenzoic acids were extracted in the usual way, except that any portion held back by manganese dioxide was freed by dissolving the latter in sulphurous acid. The *m*-nitrobenzoic acid was exhaustively separated from its isomerides by fractionation of the barium salts (the relatively insoluble *m*-salt crystallising in its characteristic needles), then of the free acids, then again of the barium salts, and so on as often as was necessary. Traces of benzoic acid, only found in Nos. 8 and 9, were determined by the loss in weight of the acid mixture when heated below  $100^{\circ}$  to constant weight, the sublimed benzoic acid being subsequently identified. Experiment 6 was carried out to ascertain whether the proportions of the isomeric nitrobenzoic acids obtained by oxidation (whereby about 80% of the theoretical quantity was recovered as crude acids) corresponded exactly with the proportions of the isomeric picrates oxidised. This was found to be the case. Corroboration was obtained by oxidising 2 g. of the picrate of the *o*-nitro-compound under identical conditions, whereby 0.579 g. of pure *o*-nitrobenzoic acid was obtained (76% of the theoretical), whereas 2.50 g. of the *m*-isomeride gave 0.76 g. of acid (79.6%); also by boiling 2 g. of *o*-nitrobenzoic acid in 240 c.c. of water with 1.5 g. of potassium hydrogen carbonate and 4 g. of potassium permanganate during 3 hours, whereby 1.789 g. (89.5%) of the unchanged acid was recovered. This proves that, in the particular method employed, undue further oxidation of *o*-, as compared with *m*- and *p*-nitrobenzoic acids, does not occur.

The yields of *m*-compound were calculated in Nos. 1, 7, 8, and 10 on the total separated picrates obtained, less a correction for any excess of picrate (0 to 0.1 g.) used beyond the normal equivalent of 97% of the theoretical quantity, and also for any traces of benzoic acid found and calculated as the picrate of the unnitrated amine. In Nos. 2, 3 and 5, where the picrates of the *op*-mixture had been worked up further for the *p*-compound before its weight was taken, and in No. 9, where this mixture was inadvertently oxidised before

No.	Amine (g.).	Acid (c.c.).		Separated picrates (g.).	m-Picrates (g.).	Picrates oxidised (g.).	m-Acid (g.).	o- plus p- Acids (g.).	Benzoic acid (g.).	m-Nitro- compound formed %.
		$\text{H}_2\text{SO}_4$ .	$\text{HNO}_3$ .							
1	1.85	11	0.8	4.65	1.87	—	—	—	—	>40.92
2	2.75	15	1.2	6.86	2.3	—	—	—	—	>33.1
3	4.647	26	2.1	11.65	3.978	—	—	—	—	>33.9
4	5.12	25	2.2	13.04	Insufficient separation	—	—	—	—	—
5	1.90	0	6	4.64	1.74	—	—	—	—	>36.45
6	—	—	—	—	—	$\left\{ \begin{array}{l} 1.50 \text{ p-} \\ 0.75 \text{ o-} \\ 0.25 \text{ m-} \end{array} \right.$	0.08	0.72	—	—
7	2.511	15	1.1	6.398	2.446	1.79	$\left\{ \begin{array}{l} 0.040 \text{ pure} \\ + 0.011 \text{ impure} \end{array} \right.$	0.440	0	43.95 $\pm$ 0.7
8	4.678	25	1.9	12.13	3.92	$\left\{ \begin{array}{l} 3.28 \\ 2.46 \end{array} \right.$	0.010 impure 0.008 impure	0.932 0.698	0.026 0.030	33.83 $\pm$ 0.35 34.30 $\pm$ 0.37
9	3.058	39.7	1.3	7.95	3.042	?	$\left\{ \begin{array}{l} 0.266 \text{ pure} \\ 0.01 \text{ impure} \end{array} \right.$	1.046	0	51.89 $\pm$ 0.23
10	3.277	42.2	1.4	8.433	3.937	2.24	$\left\{ \begin{array}{l} 0.069 \text{ pure} \\ 0.007 \text{ impure} \end{array} \right.$	0.490	0	53.51 $\pm$ 0.33

its weight had been *accurately* taken, the yield of *m*-compound was calculated on the normal yield of separated picrates amounting to 94% of the theoretical. The proportion of *m*-acid in the separated nitrobenzoic acids gave the percentage of *m*-picrate in the inseparable portion of the picrates.

The  $\pm$  corrections in the last column of the table are due to adding one-half of the small fraction of impure *m*-nitro-acid to the pure for calculation of the yield. In Nos. 9 and 10 the concentration of the amine in the sulphuric acid was accurately one-half of that obtaining in No. 7. The ammonium sulphate added in Nos. 2, 3, 4, and 8 was in excess of the amount soluble at the nitration temperature. The amount dissolved can be calculated from the following experiment: 15 c.c. of the sulphuric acid and 2.523 g. of the amine gave 17.5 c.c. of solution and 17.3 c.c. at 0°. 6.2 G. of ammonium sulphate gave a clear solution in the above liquid of 20.4 c.c. at 0°; a further 0.2 g. produced a distinct cloudiness (total volume 20.5 c.c.).

The average *m*-nitration in Nos. 9 and 10 is 52.7%. For an average degree of dissociation of 90% in nitration No. 7, Sugden's cubic root dilution law requires a yield of 50.3% of the *m*-compound in Nos. 9 and 10, whereas for 80% and 70% dissociation in No. 7, 51% and 51.9% of the *m*-compound should be obtained in Nos. 9 and 10. Walden's dilution law ( $1-\alpha = K/v^{0.45}$ ) (quoted in Walden, "Leitvermögen der Lösungen," III, 59) requires 52.5, 53.3, and 54.3%, respectively.

The authors desire to express their indebtedness to the Department of Scientific and Industrial Research for a grant to one of them (E. L. H.) which has enabled him to contribute the experimental portion of this work; also to Sir W. Bragg and the Royal Institution for placing at their disposal the facilities of the Davy Faraday Laboratory, where the work was carried out.

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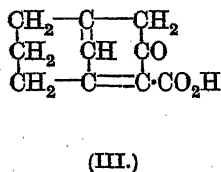
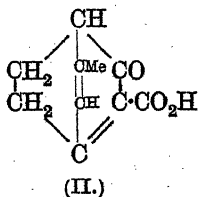
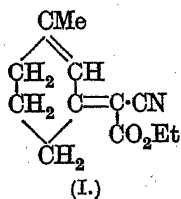
#### CCIV.—*Properties of Conjugated Compounds. Part I. Conjugative Associations in Extended "Conjugated" Systems.*

By ERNEST HAROLD FARMER and JOHN ROSS.

IN extended conjugated systems of the type  $\text{CH:CH:CH:CH:C:O}$ , the characteristic mode of terminal hydrogen addition is usually regarded as due to the conjugative coherence of all the individual saturated elements of the chain. Many reactivities of these

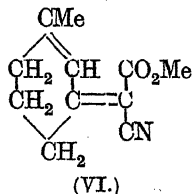
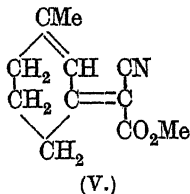
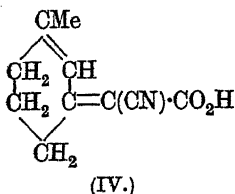
structures, however, appear to be dependent on a state of partial association in which the complex  $\text{CH}_2\text{CH}:\text{C}:\text{O}$  acts as a conjugated unit, the whole behaving as a substituted ethylene or as a  $\beta$ -substituted acrylic acid. As a means of estimating the extent of conjugative association in extended systems, an attempt has been made to examine the degree to which the behaviour of the acrylic "unit" is modified by inclusion in systems of the type in question. Since one of the most important properties of the complex is a normal capacity for change from one conjugated form to another ( $\text{CH}_2\text{CH}:\text{C}:\text{O} \rightleftharpoons :\text{C}:\text{CH}:\text{OH}$ )—a change impossible in extended systems unless the olefinic chain is branched—observations have been made in this respect, certain *cyclohexenylidenecyanoacetic* esters containing the essential structure  $\text{C} \begin{smallmatrix} \text{C}=\text{C} \\ \text{C}-\text{C} \end{smallmatrix} \text{C}=\text{C}:\text{C}=\text{O}$  being employed for the purpose.

It was shown by Knoevenagel and Mottek (*Ber.*, 1904, 37, 4464), in their investigation of the reactivity of ketones, that 1-methyl- $\Delta^1$ -*cyclohexen*-3-one reacts with ethyl cyanoacetate in the presence of piperidine, giving ethyl methyl*cyclohexenylidenecyanoacetate* (I). In accordance with the assigned constitution, this substance could be broken down by hydrolysis with caustic alkali into the original ketone and malonic acid; apparently, however, it was unsuitable for our experiments owing to the ease with which it was stated to undergo an astonishing intramolecular change. Thus, according to these authors, hydrolysis with sodium carbonate yielded an acidic compound to be represented by some such formula as (II) or (III), or one of their enolised equivalents.



Further, the silver salt of the substance yielded with methyl iodide a mixture of isomeric esters or ethers for the isomerism of which it was difficult to account. The formulæ assigned were necessitated solely by the analytical results; there was nothing in the behaviour of the substance itself to suggest the presence of the aromatic nucleus which these formulæ imply. Consequently, in reviewing the evidence, the suspicion arose that the acidic compound was a nitrogenous substance, and, if formula (I) were correct, was actually the normal hydrolysis product (IV). Repetition of Knoevenagel

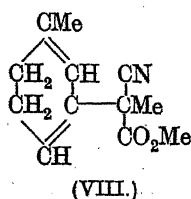
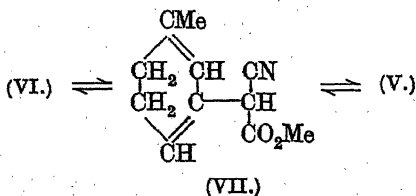
and Mottek's work confirmed this view, thus rendering possible the study of the methylcyclohexenyldenecyanoacetic esters.



The ethyl ester was very readily obtained and was converted by alcoholic alkali into an acid agreeing with formula (IV) analytically, and in melting point and general properties with Knoevenagel and Mottek's supposed dicyclic compound. This rather intractable acid did not appear homogeneous, but could not be separated into components by fractional crystallisation. Esterification, however, yielded the two isomeric methyl esters mentioned above.

Formula (IV) at once suggests the possibility of geometrical isomerism about the extracyclic double bond, and the two isomerides found might be regarded as the maleinoid and fumaroid forms (V and VI). This being so, these two solid methyl esters should be directly obtainable by the condensation of methyl cyanoacetate with the ketone. When this was done, the excellent yield of the two methyl esters obtained left no doubt as to their monocyclic constitution.

As the isomerides or tautomerides concerned in mobility of the  $\alpha\beta$ - $\beta\gamma$  type are usually brought into equilibrium in the presence of alkalis or sodium alkyl oxides, the two methyl methylcyclohexenyldenecyanoacetates were separately treated with alcoholic sodium methoxide. In each case, a similar mixture of three esters was obtained from the product. Two of these were the esters (V) and (VI), and the third must be regarded as the methyl methylcyclohexadienylcyanoacetate (VII). Subsequently this was shown to yield a similar mixture of three isomerides on treatment with sodium methoxide. Since in all three mixtures the proportions of the

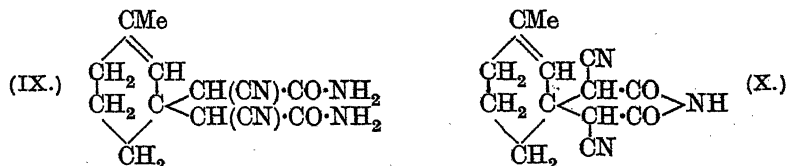


components appeared identical, there is little doubt that an equilibrium holds. Caustic alkali exerted a similar influence during the

hydrolysis of these esters, as was shown by the melting point of the acid mixture obtained and by the nature of the mixture of esters obtained on re-esterification; further, upon repetition of these processes with larger amounts of the ethyl ester first obtained, the third methyl ester was isolated in this case also.

Each of the three esters gave a distinctive dibromide and each could be methylated precisely as the various *cyclopentenyl*- and *cyclohexenyl*-cyanoacetic esters and their tautomerides (Harding and Haworth, J., 1910, 97, 490; Birch and Kon, J., 1923, 123, 2440), the product in all cases being one and the same methyl derivative (VIII).

In attempts to prepare the cyanoacetamides of the isomeric esters by means of aqueous ammonia, each gave rise to a dicyanoacetamide (IX) and the ammonium salt of the imide (X), both being identical with the compounds directly obtainable from the ketone and cyanoacetic ester by the Guareschi synthesis. Such syntheses resulting from the reversion of a portion of the cyclic ester into its generators, with the subsequent addition of the liberated cyanoacetic ester (or amide) to the undecomposed portion, have recently been observed in other series (private communication by Miss W. Kilroy).



Among the small portions of ester recovered in these reactions, isomerides other than the original one were obtained. Interconversion of the esters could be secured only by the use of an alkaline equilibrating agent; thus the passage from a fumaroid to a maleinoid form was only possible by way of the third (*cyclohexadienyl*-) form, and in the original condensation of the ketone and methyl cyanoacetate two and only two forms were obtained.

In estimating the effect of conjugative association on the incorporation of the group  $\text{CH}:\text{CH}:\text{C}:\text{O}$  in a larger unit, it is convenient to compare the results obtained above with the evidence furnished by substances containing no double bonds other than those of the acrylic system. Among the latter, considerable, and at present inexplicable, variations occur in the speed of attainment and in the position of equilibrium. In some cases, the  $\alpha\beta$ - and  $\beta\gamma$ -forms are readily isolable and undergo appreciable interconversion only in the presence of a reagent like sodium alkyl oxide; in the limiting cases, isomerisation is so rapid (even in absence of a reagent) and the position of equilibrium favours so strongly one form or the other

that the separation of individuals has been impossible.\* In the cyclohexenylidene esters described above, the acrylic group seems to be preserved as a definite unit. Change of the  $\alpha\beta$ - $\beta\gamma$  type, which might conceivably have been suppressed, is here of normal and intermediate character; and in so far as this is the case there is no positive evidence of any considerable tendency for the extended system, of which the acrylic group is a part, to act persistently as a completely conjugated unit.

#### EXPERIMENTAL.

*Condensation of Methyl Cyanoacetate with 1-Methyl- $\Delta^1$ -cyclohexen-3-one.*—A mixture of the ketone (110 g.), the ester (100 g.), and piperidine (10 c.c.) was heated at 120—125° for 6 hours. The cooled product, upon the surface of which a thin aqueous layer had formed, was diluted with ether and thoroughly washed, first with dilute sulphuric acid and then with dilute sodium carbonate solution. The dried ethereal solution was distilled, finally at a very low pressure (the amount of undecomposed material passing over at 1 mm. was double that at 10 mm.); the fraction, b. p. 165—175°/2 mm., solidified on cooling (yield 70%).

A considerable portion of this solid dissolved in boiling petroleum (b. p. 40—60°). The solution deposited one isomeride of *methyl 1-methyl- $\Delta^1$ -cyclohexenylidene-3-cyanoacetate* in large, needle-shaped prisms, m. p. 74°; these were sometimes colourless, but often had a deep yellow colour which was removed by boiling in petroleum solution with animal charcoal (Found: C, 68.95; H, 6.9; N, 7.5.  $C_{11}H_{13}O_2N$  requires C, 69.05; H, 6.85; N, 7.3%).

The petroleum mother-liquor, after concentration and cooling, deposited flat, colourless prisms, m. p. 60°. This substance, isomeric with that described above (the two are regarded as isomerides of the fumaroid-maleinoid type), represented about 6% of the ester mixture (Found: C, 69.05; H, 6.9; N, 7.45%).

The portion of the ester mixture undissolved by boiling petroleum crystallised from methyl alcohol-petroleum in colourless, hexagonal prisms, m. p. 88°. The nature of this stable, highly nitrogenous substance, which is readily obtainable from the cyanoacetic ester and piperidine alone, has not been determined (Found: C, 63.1; H, 8.0; N, 17.7%).

\* The strictly comparable cyclohexylidene- and cyclopentylidene-cyanoacetic esters are liquids (Birch, Kon, and Norris, J., 1923, 123, 1368) and from the details published it is evident that both the position of equilibrium and the isolability of the separate forms are uncertain. In the present case, equilibrium is attained when the material is divided between the cyclohexylidene and the cyclohexenylidene form in the approximate ratio of 3 : 10.



*Condensation of Ethyl Cyanoacetate with 1-Methyl- $\Delta^1$ -cyclohexen-3-one.*—This condensation, effected by Knoevenagel and Mottek's method (*loc. cit.*), produced an oil from which, by distillation at 1 mm. pressure and refractionation, a mixture of esters, b. p.  $190^{\circ}/16$  mm., which solidified on cooling, was obtained. The main part of this mixture melted at  $58^{\circ}$  after recrystallisation from light petroleum. This substance, doubtless one form of ethyl methylcyclohexenylidenecyanoacetate, was used for the repetition of Knoevenagel and Mottek's experiments (Found: C, 70.0; H, 7.5; N, 7.05. Calc. for  $C_{12}H_{15}O_2N$ : C, 70.2; H, 7.4; N, 6.85%).

*Equilibration by Alcoholic Caustic Alkali.*—*Hydrolysis of methylcyclohexenylidenecyanoacetic esters.* The ethyl ester was not appreciably hydrolysed on boiling for 12 hours with 15% hydrochloric acid and was only slowly affected by boiling with sodium carbonate solution in the manner described by Knoevenagel and Mottek. Since prolonged treatment with caustic alkali caused degradation, the ester was boiled for 30 minutes with 10% aqueous-alcoholic caustic potash (alcohol: water = 3:1). The deep brown solution so obtained was cooled, and the hydrolysis product separated by the usual methods into neutral and acidic portions. The acidic portion was a very sticky, brown solid which was recrystallised several times from benzene, decolorised by animal charcoal, and recrystallised from acetone. This acid, which was not homogeneous in crystalline form, melted at  $149^{\circ}$  (Found: C, 67.6; H, 6.3; N, 7.9; *M*, monobasic, 174. Calc. for  $C_{10}H_{11}O_2N$ : C, 67.8; H, 6.25; N, 7.9%; *M*, 177.1). The ammonium salt was obtained, from the acid and ammonia in ether, as a colourless, crystalline precipitate, which was dried in a vacuum. The silver salt was precipitated as a pale yellow powder from an aqueous solution of the ammonium salt by silver nitrate.

*Separation of the isomeric esters.* The mixture of methyl esters, b. p.  $180$ — $185^{\circ}/17$  mm., obtained by boiling the silver salt with alcoholic methyl iodide was crystallised from petroleum. The characteristic, needle-like crystals of methyl methylcyclohexenylidenecyanoacetate, m. p.  $74^{\circ}$ , separated first; then, after concentration, the geometrical isomeride, m. p.  $60^{\circ}$ , was obtained in large, hexagonal plates. (Both of these were shown by analysis and by direct comparison to be identical with the respective esters described above.) Finally, when the mother-liquor had been evaporated almost to dryness, crystals of methyl 1-methyl- $\Delta^{1:3}$ -cyclohexadienyl-3-cyanoacetate were obtained. These, after recrystallising several times from strongly-cooled methyl alcohol-petroleum, were obtained in colourless needles, m. p.  $42^{\circ}$  (Found: C, 69.1; H, 7.0; N, 7.5.  $C_{11}H_{13}O_2N$  requires C, 69.05; H, 6.9; N, 7.35%).

The proportions in which the three esters were obtained were (m. p.  $74^{\circ}$ ) : (m. p.  $60^{\circ}$ ) : (m. p.  $42^{\circ}$ ) = 4 : 1 : 1.6.

*Equilibration by Sodium Alkylloxide.*—A mixture of the ester, m. p.  $74^{\circ}$  (3 g.) and sodium methoxide (1 mol.) in cold methyl alcohol was kept for one hour and then poured into water. The mixture of solid esters (2 g.) obtained by extracting the product with ether yielded, on fractional crystallisation, the three isomeric esters in the approximate proportions 4.2 : 1 : 1.5. Nearly a third of the material suffered hydrolysis during the process.

Similar results were obtained with the other two isomerides.

*Methylation of the Isomeric Esters.*—An equilibrated mixture obtained as described above was heated on a water-bath with an excess of methyl iodide for 30 minutes. The cooled solution was poured into ice-water, and the product extracted with ether. The extract was washed in turn with dilute acid and sodium carbonate solution and dried. Evaporation of the ether yielded an oil two-thirds of which distilled at  $160$ — $165^{\circ}/10$  mm. On redistillation it was obtained as a colourless, mobile liquid, b. p.  $160^{\circ}/11$  mm. This substance, from its analysis and ready conversion into the corresponding acetonitrile, must be regarded as *methyl 1-methyl- $\Delta^{1:3}$ -cyclohexadienyl-3- $\alpha$ -cyanopropionate* (VIII) (Found : C, 69.95; H, 7.5; N, 7.3.  $C_{12}H_{15}O_2N$  requires C, 70.2; H, 7.4; N, 6.9%).

*Bromination of the Isomeric Methyl Methylcyclohexenylidenecyanoacetates.*—The esters, m. p.  $74^{\circ}$  and  $60^{\circ}$ , yielded, on bromination (1 mol.) in cold chloroform, *dibromides* which crystallised from alcohol-petroleum in large, colourless prisms, m. p.  $77^{\circ}$  (Found : Br, 45.2%), and fine needles, m. p.  $65^{\circ}$  (Found : Br, 45.3.  $C_{11}H_{13}O_2NBr$  requires Br, 45.5%) respectively. The ester, m. p.  $42^{\circ}$ , similarly yielded a yellow, oily dibromide (Found : Br, 44.8%).

These dibromides readily lost hydrogen bromide on treatment with diethylamine, but the products were all liquid and could not be satisfactorily reduced by any of the reagents employed.

*Decarboxylation of the Cyano-esters.*—Decarboxylation of (VIII) by Birch and Kon's method (*loc. cit.*, p. 1374) gave, in good yield, *1-methyl- $\Delta^{1:3}$ -cyclohexadienyl-3-propionitrile* as a colourless, mobile liquid, b. p.  $126^{\circ}/11$  mm. (Found : C, 81.9; H, 9.0; N, 9.0.  $C_{10}H_{13}N$  requires C, 81.6; H, 8.9; N, 9.5%).

The purified hydrolysis product of methyl (or ethyl) methylcyclohexenylidenecyanoacetate (p. 1575) yielded, on heating with water at  $180^{\circ}$  or on boiling for 30 minutes with 15% hydrochloric acid, a light, neutral oil which, after extraction, drying, and distillation, was obtained as a colourless, mobile, highly refractive liquid, b. p.  $105$ — $110$  mm. (Found : C, 80.8; H, 8.3; N, 10.2.  $C_9H_{11}N$  requires C, 81.1; H, 8.3; N, 10.5%).

*Action of Ammonia upon the Three Isomeric Esters.*—The methyl ester, m. p.  $74^{\circ}$  (3 g.), gradually dissolved in concentrated aqueous ammonia, and after 12 hours large crystals, m. p.  $273^{\circ}$ , of 1-methyl- $\Delta^1$ -cyclohexene-3 : 3-dicyanoacetamide (IX) were deposited. A second crop consisted of this substance and the ammonium salt of the cyanimide (X). The latter had m. p.  $188^{\circ}$  (Found : C, 60.1; H, 6.4; N, 21.3.  $C_{13}H_{16}O_2N_4$  requires C, 59.95; H, 6.2; N, 21.5%) and yielded, on acidification of its aqueous solution, the free imide, a white, crystalline powder, m. p.  $195^{\circ}$  (Found : N, 17.1.  $C_{13}H_{13}O_2N_3$  requires N, 17.3%). The dicyanoacetamide, which was insoluble in all the ordinary solvents, was washed in turn with boiling alcohol and boiling water and then had m. p.  $275^{\circ}$  (Found : C, 59.85; H, 6.2; N, 21.4.  $C_{13}H_{16}O_2N_4$  requires C, 59.95; H, 6.2; N, 21.5%). The yields of the condensation products corresponded with the explanation of their formation given in the introduction.

The esters, m. p.  $60^{\circ}$  and m. p.  $42^{\circ}$ , also gave on similar treatment the same two compounds (m. p.  $188^{\circ}$  and m. p.  $275^{\circ}$ ). The quantities of the cyclic imide and dicyanoacetamide produced varied in the different experiments, but the total amount was constant.

*Condensation of Methyl Methylcyclohexenylidenecyanoacetate with Methyl Cyanoacetate.*—To a solution of the ester, m. p.  $74^{\circ}$  (5 g.) and methyl cyanoacetate (2.5 g.) in cold alcohol, ammoniacal alcohol (10 c.c., saturated at  $-10^{\circ}$ ) was added, and the mixture kept at  $0^{\circ}$  for 2 days, much crystalline matter separating. The ammonium salt of the cyclic imide and the dicyanoacetamide described above were thus obtained in 68% yield.

*Condensation of Methylcyclohexenone and Ethyl Cyanoacetate.*—A mixture of methylcyclohexenone (4 g.), ethyl cyanoacetate (8.5 g.), and ammoniacal alcohol (18 c.c., saturated at  $-10^{\circ}$ ) was kept at  $0^{\circ}$  in a closed bottle. The crystals deposited after 1 day consisted almost entirely of cyanoacetamide, but after 3 days 5.5 g. of the almost pure ammonium salt of the imide (X) were obtained.

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CCV.—*The Isomerism of the Styryl Alkyl Ketones.*  
*Part III. Methoxy-2- and 4-hydroxystyryl Alkyl Ketones.*

By ALEXANDER MCGOOKIN and DONALD JAMES SINCLAIR.

IN order to confirm the results of the investigations on the isomerism and behaviour towards alkali of the hydroxystyryl alkyl ketones (J., 1924, 125, 2099; 1925, 127, 2539) various derivatives of 2-hydroxystyryl methyl ketone and analogous compounds have been prepared and examined.

5-Methoxy-2-hydroxystyryl methyl ketone (Heilbron and Whitworth, J., 1923, 123, 238), like the 2-hydroxy-compound, exists in a yellow and a colourless form of identical m. p. and is partly converted into the red sodium salt of 5 : 5'-dimethoxy-2 : 2'-dihydroxydistyryl ketone in alkaline solution. This change occurs instantly with the yellow isomeride, but only very slowly with the colourless modification; the colourless form of 2-hydroxystyryl methyl ketone also develops the usual red colour in similar circumstances.

The colourless form of 4-methoxy-2-hydroxystyryl methyl ketone has been isolated; it is stable in air and resembles the colourless form of 2-hydroxystyryl methyl ketone in properties. The yellow form (Heilbron and Whitworth, *loc. cit.*) has not been obtained pure and is under investigation.

The yellow crystalline condensation product, m. p. 83°, of 3-methoxysalicylaldehyde and acetone obtained by Heilbron and Whitworth (*loc. cit.*), and regarded by them as  $\beta$ -hydroxy- $\beta$ -3-methoxy-2-hydroxyphenylethyl methyl ketone, has also been described by Nomura and Nozawa (*Sci. Rep. Tôhoku Imp. Univ.*, 1918, 7, 79), who consider it a hydrate of 3-methoxy-2-hydroxystyryl methyl ketone. Further examination indicates that it is a hydrate rather than an aldol. In addition to the benzoyl derivative of 3-methoxy-2-hydroxystyryl methyl ketone already obtained from it by Heilbron and Whitworth (*loc. cit.*) an *acetyl* derivative of the unsaturated ketone has been prepared. Both compounds, on hydrolysis, yield the hydrated substance. Moreover, condensation of this compound with 3-methoxysalicylaldehyde produces the symmetrical distyryl ketone. Again, crystallisation of the hydrated substance from dry benzene yields, as a second crop, colourless needles which, on removal of the solvent, immediately absorb water to form the original yellow compound of m. p. 83°. 3-Methoxy-2-hydroxystyryl methyl ketone, however, could not be isolated. From the compound of m. p. 83°, by crystallisation from an anhydrous solvent, Nomura and Nozawa (*loc. cit.*) obtained

an unsaturated ketone of m. p. 77—77·5°. This m. p. for 3-methoxy-2-hydroxystyryl methyl ketone is anomalous in three respects : (i) all ketones of this type melt at about 130°; (ii) removal of water from an aldol or a hydrate invariably causes a rise in m. p.; (iii) the symmetrical distyryl ketone has a normal m. p.

In Part I the compound of m. p. 83° was assumed to have the aldol structure, and the fact that it could not be isomerised was taken as evidence of the geometric nature of the isomerism of this class of ketones. In view of the present observations this evidence cannot be taken as conclusive.

The yellow form of 3-methoxy-4-hydroxystyryl methyl ketone (Francesconi, *Gazzetta*, 1908, 38, ii, 70; McGookin and Heilbron, J., 1924, 125, 2104) is peculiar in being exceedingly stable, resisting isomerisation except by extreme methods. When, however, concentrated alkali is added to its alkaline solution, the salt precipitated is that of the colourless form. Hence it is assumed that the salts of both isomerides are in equilibrium in alkaline solution.

The yellow form of 3-methoxy-4-hydroxystyryl methyl ketone changes on fusion into the colourless modification of the same m. p.—a similar change doubtless accounts for the identity of the m. p.'s of each pair of isomerides throughout this series of ketones. Both forms of this substance resemble those of 2-hydroxystyryl methyl ketone by dissolving in alkali, the yellow form to yield a red solution and the colourless isomeride to give a yellow solution which assumes a red colour on standing. In both instances the red colour is due to the sodium salt of 3 : 3'-dimethoxy-4 : 4'-dihydroxydistyryl ketone. Hence styryl methyl ketones are capable of condensing to a slight extent with 4-hydroxyaldehydes in the presence of alkalis (compare Buck and Heilbron, J., 1922, 121, 1095).

#### EXPERIMENTAL.

**5-Methoxy-2-hydroxystyryl Methyl Ketone.**—The colourless modification was obtained, by boiling the yellow isomeride (Heilbron and Whitworth, *loc. cit.*) with water containing a trace of acid, in needles, m. p. 124°, soluble in alcohol or benzene. It dissolves in alkali to a yellow solution which develops a deep red colour after 12 hours (Found : C, 68·5; H, 6·3.  $C_{11}H_{12}O_3$  requires C, 68·7; H, 6·3%).

**5 : 5'-Dimethoxy-2 : 2'-dihydroxydistyryl Ketone.**—When 40% sodium hydroxide (10 c.c.) was added to a solution of the yellow isomeride of 5-methoxy-2-hydroxystyryl methyl ketone (2 g.) in 20% sodium hydroxide (30 c.c.), lustrous, green needles separated. An aqueous solution of these, on acidification, gave the distyryl ketone (1·2 g.), which crystallised from alcohol in orange needles,

m. p. 158°, soluble in acetone but almost insoluble in benzene (Found: C, 69.6; H, 5.6.  $C_{19}H_{18}O_5$  requires C, 69.9; H, 5.5%).

**4-Methoxy-2-hydroxystyryl Methyl Ketone.**—The following is the best modification of Heilbron and Whitworth's method. To a solution of 4-methoxysalicylaldehyde (9 g.) and acetone (16 g.) in alcohol (100 c.c.), sodium hydroxide (200 c.c. of 20%) was added. After 3 days the red mixture was diluted with water (1000 c.c.), cooled to 0°, and almost neutralised with dilute sulphuric acid (rise of temperature or excess of acid caused the production of tar). The product (10 g.) was crystallised from benzene and from chloroform-hexane and obtained in colourless needles, m. p. 131°. It was readily soluble in alkali to a yellow solution which developed a deep red colour after 12 hours.

**4:4'-Dimethoxy-2:2'-dihydroxydistyryl Ketone.**—A mixture of 2 mols. of 4-methoxysalicylaldehyde (10 g.), 1 mol. of acetone (2 g.), and alcohol (40 c.c.) was treated with sodium hydroxide (250 c.c. of 20%) and warmed on the water-bath for 10 minutes. The deep red solution deposited, after 12 hours, lustrous green needles of the sodium salt of the distyryl ketone. From an aqueous solution of this, almost neutralised at 0°, the ketone was precipitated as a yellow solid. It crystallised from cold aqueous alcohol in brown plates, m. p. 170°, soluble in alcohol, but almost insoluble in benzene. It is unstable and produces a red solution with an intense green fluorescence when warmed in alcohol (Found: C, 69.6; H, 5.6.  $C_{19}H_{18}O_5$  requires C, 69.9; H, 5.5%).

**3-Methoxy-2-hydroxystyryl Methyl Ketone Hydrate (?)**.—This compound (Heilbron and Whitworth, *loc. cit.*) formed yellow plates, m. p. 83°, from aqueous alcohol. It crystallised from dry benzene in similar yellow plates, but the second crop of crystals consisted of colourless, hygroscopic needles. These dissolved in alkali to form an orange-red solution which developed the usual deep red colour on standing.

**3-Methoxy-2-acetoxystyryl Methyl Ketone.**—The hydrated compound (10 g.) was boiled for an hour with acetic anhydride (150 c.c.), the hot solution poured into an excess of water, and almost neutralised with sodium carbonate. The precipitate produced (10 g.) crystallised from alcohol in colourless needles, m. p. 91°, soluble in benzene or hot water (Found: C, 66.4; H, 6.1.  $C_{13}H_{14}O_4$  requires C, 66.6; H, 6.0%).

**3:3'-Dimethoxy-2:2'-dihydroxydistyryl Ketone.**—The sodium salt that separated after 24 hours from a solution of 3-methoxysalicylaldehyde (50 g.) in acetone (80 g.) and sodium hydroxide (600 c.c. of 2.5%) to which 10% sodium hydroxide (240 c.c.) had been added was dissolved in water and acidified. The ketone precipitated

crystallised from aqueous alcohol in orange needles, m. p.  $182^{\circ}$  (Found: C, 69.6; H, 5.5.  $C_{19}H_{18}O_5$  requires C, 69.9; H, 5.5%).

**3-Methoxy-4-hydroxystyryl Methyl Ketone.**—A solution of vanillin (50 g.) in acetone (120 c.c.) and alcohol (50 c.c.) was treated with sodium hydroxide (100 c.c. of 20%) and kept for 12 hours. Long, yellow needles of the *sodium* salt of the colourless isomeride were produced; the *ketone* obtained from these crystallised from aqueous alcohol in colourless needles, m. p.  $129^{\circ}$ , soluble in acetone or benzene. It dissolved in alkali to a yellow solution which turned red after 12 hours.

**3:3'-Dimethoxy-4:4'-dihydroxydistyryl Ketone.\***—(a) On boiling, a solution of the preceding colourless isomeride (25 g.) in sodium hydroxide (200 c.c. of 20%) became deep red and acetone was evolved. When the evolution of this had ceased, after 15 minutes, the solution was cooled, and sodium hydroxide (40%) added until a precipitate formed. Lustrous green needles of the *sodium* salt of the distyryl ketone slowly separated. The *ketone* obtained from these crystallised from chloroform in pale yellow needles, m. p.  $142^{\circ}$  (Found: C, 69.6; H, 5.6.  $C_{19}H_{18}O_5$  requires C, 69.9; H, 5.5%).

This compound was very soluble in alcohol or acetone, moderately easily soluble in chloroform, but almost insoluble in benzene. It forms an orange-red *hydrate*, m. p.  $121^{\circ}$ , containing one molecule of water when crystallised from an aqueous solvent (Found: C, 65.8; H, 5.9.  $C_{19}H_{18}O_5 \cdot H_2O$  requires C, 66.2; H, 5.8%). The hydrate loses water when heated in a steam-oven or crystallised from a non-aqueous solvent.

(b) A better yield (15 g.) of the distyryl ketone was obtained by gradually adding concentrated hydrochloric acid (50 c.c.) to a solution of vanillin (25 g.) in acetone (90 c.c.) cooled in a freezing mixture. A dark violet-red coloration was observed and from the mixture, kept at  $0^{\circ}$  for 4 days, green-black crystals separated. These were filtered off, washed well with ether, and decomposed by dissolution in excess of sodium hydroxide (10%). The free distyryl ketone was obtained from this solution as before.

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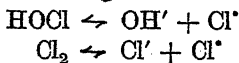
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\* This compound has recently been prepared by Nomura and Hotta (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, 14, 119).

CCVI.—*The Halogenation of Phenols.*

By FREDERICK GEORGE SOPER and GILBERT FREEMAN SMITH.

THE iodination of phenols has been investigated by Cofman (J., 1919, 115, 1040), who concluded that the active iodinating agent was hypoiodous acid, free iodine having apparently no direct iodinating effect. Similar views were held on the mechanism of bromination (Baines, J., 1922, 121, 2810), but recently Francis (J. Amer. Chem. Soc., 1925, 47, 2340) has shown that bromine is a more active brominating agent than hypobromous acid. Both Cofman and Francis are of the opinion that probably the only active halogenating agent is the positive halogen ion. This conclusion can be tested using halogens and hypohalous acids, since, although the actual degrees of ionisation of these substances into positive halogen ions (Stieglitz, J. Amer. Chem. Soc., 1901, 23, 796) are not known—except in the case of hypoiodous acid (Murray, J., 1925, 127, 882)—their relative ionisations may be calculated from other data. For, assuming the existence of such equilibria as



then

$$\frac{K_{\text{HOCl}}}{K_{\text{Cl}_2}} = \frac{[\text{OH}'][\text{Cl}']}{[\text{HOCl}]} \bigg/ \frac{[\text{Cl}'][\text{Cl}']}{[\text{Cl}_2]} = \frac{[\text{Cl}_2][\text{OH}'][\text{H}']}{[\text{Cl}']^2[\text{HOCl}][\text{H}']} = \frac{K_w}{K_s},$$

where  $K_s$  is the hydrolysis constant of chlorine (Jakowkin, Z. physikal. Chem., 1899, 29, 613) and equals  $4.84 \times 10^{-4}$ . Similar expressions hold for bromine and for iodine, the hydrolysis constants being  $5.2 \times 10^{-9}$  and  $3 \times 10^{-13}$  respectively (Bray and Connolly, J. Amer. Chem. Soc., 1911, 33, 1485; Bray, *ibid.*, 1910, 32, 932). On substituting these values in the above expression, the ionisation constants of chlorine and hypochlorous acid will be in the ratio  $4.5 \times 10^{10}$  to 1; and one would expect that their chlorinating efficiencies would be in the same ratio. The corresponding values for bromine and iodine and their hypohalous acids are  $5 \times 10^5$  and 30 respectively. Thus, whilst hypochlorous acid would have little chlorinating effect in comparison with free chlorine, we should expect the effects of iodine and hypoiodous acid to be of the same order of magnitude.

In order to test this theory of halogenation by positive halogen ion, the chlorination of phenols has been studied, using hypochlorous acid and chlorine as chlorinating agents. The much greater stability of hypochlorous acid (as compared with hypobromous and hypoiodous acids) has allowed of a sharp differentiation between the mechanisms of substitution of phenols by these two chlorinating agents.



The mechanism of the interaction with hypochlorous acid was investigated by the isolation method. The reaction speed is approximately proportional to the phenol and hypochlorous acid concentrations, and is greatly affected by the alkalinity or acidity of the mixture. In acid and in dilute alkaline solutions (hydroxyl-ion concentration in the neighbourhood of  $10^{-7}$ ) the reaction speed increases in direct proportion to the hydroxyl-ion concentration until it becomes too rapid for measurement. In more strongly alkaline solution (hydroxyl-ion concentration about  $10^{-2}$ ), the speed decreases to measurable dimensions, and is now inversely proportional to the hydroxyl-ion concentration.

These facts can be interpreted in two ways. Interaction may take place either between the phenol molecule and the hypochlorite ion or between hypochlorous acid and the phenoxide ion, the reaction speed being given by the alternative equations

$$v = k_2'[\text{OCl}'][\text{PhOH}] \quad \dots \quad (1)$$

$$v = k_2[\text{HOCl}][\text{PhO}'] \quad \dots \quad (2)$$

On both hypotheses addition of alkali, by causing increased ionisation, would first increase and then decrease the speed as was observed. The alternative hypotheses cannot, however, be differentiated by studying the reaction between a simple phenol and hypochlorous acid, since it follows from the ionic equilibria of hypochlorous acid and a phenol that

$$[\text{OCl}'][\text{PhOH}]/[\text{HOCl}][\text{PhO}'] = K_a'/K_a'' = \text{constant},$$

where  $K_a'$  and  $K_a''$  are the respective ionisation constants. It is obvious that any test of the first explanation will be equally satisfactory when applied to the second explanation, if it is based on the constancy of  $k_2$  or  $k_2'$ .

It is shown later from other evidence that the mechanism involves the phenoxide ion and hypochlorous acid. The constant  $k_2$ , rather than  $k_2'$ , is therefore calculated in the following preliminary proof of the correctness of the suggested mechanism of the reaction.

The calculation of the velocity coefficient in the presence of excess of alkali involves the hydrolysis constant of sodium hypochlorite (Soper, J., 1924, 125, 2227), since the hypochlorous acid and the phenol are present almost entirely as ions, sodium hypochlorite and phenoxide in the presence of  $N/10$ -hydroxyl-ion being hydrolysed only to the extent of 0.1 and 0.001% respectively.

$$\begin{aligned} dx/dt &= k_2[\text{HOCl}][\text{PhO}'] = k_2K_h'/[\text{OH}'] \cdot [\text{OCl}'][\text{PhO}'] \\ &= k_2K_h'/[\text{OH}'] \cdot (b-x)(a-x) \end{aligned}$$

or

$$k_2K_h' = \frac{1}{i(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

where  $K_h'$  represents the hydrolysis constant of the hypochlorite.

The terms  $a - x$  and  $b - x$  in this equation represent the activities of the hypochlorite and phenoxide ions which are some fraction of the concentrations of sodium hypochlorite and phenoxide, respectively, dependent on the ionic strength (Lewis and Randall, "Thermodynamics," 1924) of the mixture. In the absence of data on the activities of these ions, we have taken them as equal to the concentrations of their respective salts. The effective concentration of the hydroxyl ion was taken as the product of the concentration of free base and its appropriate activity coefficient. The results obtained at 25.0° with *p*-cresol and alkaline hypochlorite are in Table I, where time is shown in minutes.

TABLE I.

[HOCl] = $10^{-3}$ ; [p-cresol] = $2 \times 10^{-3}$ ; [NaOH] = 0.019; $\gamma[\text{OH}'] = 0.01424$ .			[HOCl] = $10^{-3}$ ; [p-cresol] = $2 \times 10^{-3}$ ; [NaOH] = 0.038; $\gamma[\text{OH}'] = 0.02904$ .		
Time.	$[\text{OCl}'] \times 10^4$ . $k_2 \times 10^{-5}$ .		Time.	$[\text{OCl}'] \times 10^4$ . $k_2 \times 10^{-5}$ .	
0	8.28	—	0	8.90	—
4.03	5.51	8.59	3.40	7.44	8.39
6.78	4.26	8.75	7.88	5.95	8.59
9.67	3.19	9.26	11.65	4.93	8.82
13.08	2.13	10.3	15.75	4.03	9.10
17.15	1.48	10.5	21.03	3.07	9.60
			27.23	2.24	10.1

Another experiment, in which  $[\text{HOCl}] = 10^{-3}$ ;  $[\text{p-cresol}] = 10^{-2}$ ;  $[\text{NaOH}] = 10^{-1}$ ;  $\gamma[\text{OH}'] = 0.0712$ , gave values of  $k_2 \times 10^{-5}$  which gradually decreased from 9.37 to 8.70.

The velocity coefficient can also be calculated from measurements of the reaction speed in water. The ionisation constants of hypochlorous acid (Soper, *loc. cit.*) and of *p*-cresol (Boyd, J., 1915, 107, 1538) are  $1.0 \times 10^{-8}$  and  $0.67 \times 10^{-10}$ , respectively. The hydrogen-ion concentration will therefore be governed by the hypochlorous acid, and in *M*/1000-solution will be  $3.1 \times 10^{-6}$ , but will increase slightly in concentrated solutions of *p*-cresol. During the reaction, hypochlorous acid disappears, and it might be anticipated that the acidity of the mixture would diminish. Actually indicators show that at the conclusion of the reaction the acidity has slightly increased. This is probably due to a very slight reduction of the hypochlorous acid, for even traces of hydrochloric acid would materially affect the hydrogen-ion concentration. In the calculations which follow, the hydrogen-ion concentration has been regarded as constant.

In aqueous solution both hypochlorous acid and *p*-cresol are mainly un-ionised. The concentration of the phenoxide-ion will be

determined by the acidity of the solution and the ionisation constant of the cresol, thus

$$[\text{R}\cdot\text{O}'] = K_a''[\text{R}\cdot\text{OH}]/[\text{H}'].$$

The velocity is given by

$$dx/dt = k_2[\text{R}\cdot\text{O}'][\text{HOCl}] = k_2[\text{HOCl}] \cdot K_a''[\text{R}\cdot\text{OH}]/[\text{H}'] = \frac{k_2 K_a''(b-x)(a-x)}{[\text{H}']}$$

$$\text{or} \quad \frac{k_2 K_a''}{[\text{H}']} = k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}.$$

Mixtures were used in which the hypochlorous acid was  $M/1000$ , and the *p*-cresol concentration varied from  $10^{-3} M$  to  $4 \times 10^{-2} M$ . Table II shows one experiment in detail, and Table III summarises all the experiments.

Table II.

$$[\text{R}\cdot\text{OH}] = 10^{-2}; [\text{HOCl}] = 10^{-3}.$$

Time.	$[\text{HOCl}]$ $\times 10^3$ .	$k_2 K_a''/$ $[\text{H}']$ .
0	0.821	—
3.60	0.583	9.81
6.85	0.449	9.16
7.97	0.402	9.39
9.57	0.362	8.96

TABLE III.

$[\text{R}\cdot\text{OH}]$ $\times 10^3$ .	$k$ .	$[\text{H}']$ $\times 10^3$ .	$k_2 \times 10^{-5}$ .
1	19.5	3.17	9.23
2	13	3.19	6.19
5	10	3.22	4.81
10	9.3	3.26	4.53
20	8.8	3.37	4.43
40	8.0	3.55	4.24

The higher value for the velocity coefficient when equimolar quantities of hypochlorous acid and cresol interact is due to the chlorination of the chlorocresol formed. The average value for the velocity coefficient in aqueous solution when excess of the cresol is present may be taken as  $5 \times 10^5$ , as compared with the value  $10 \times 10^5$  in alkaline solution. The lower value obtained in water is probably to be attributed partly to the fact that activities are not accurately represented by concentrations, partly to some uncertainty in the ionisation constants concerned, and partly to the effect of the presence of other substances on the degrees of ionisation.

The addition of acids, with the exception of hydrochloric acid, decreased the observed speed. The effect of hydrochloric acid doubtless depends on the formation of chlorine, and is dealt with in Section 2.

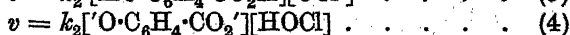
The comparison of velocity coefficients calculated from the observed speeds in aqueous and in strongly alkaline solution is a stringent test of the mechanism, as it involves concentrations of the reacting species which differ by several thousand times in the two cases. This test has been repeated for other phenols. The results are summarised in Table IV.

TABLE IV.

[R·OH].	[HOCl].	[H·] × 10 <sup>6</sup> .	[NaOH].	γ[OH·].	k <sub>2</sub> .
<i>Phenol</i> (K <sub>a</sub> '' = 1.1 × 10 <sup>-10</sup> ).					
0.005	0.0010	3.24	—	—	3.24 ± 0.27 × 10 <sup>5</sup>
0.010	0.0010	—	0.10	0.0712	3.34 ± 0.07 × 10 <sup>5</sup>
0.010	0.0010	—	0.04	0.0249	3.21 ± 0.08 × 10 <sup>5</sup>
<i>o-Chlorophenol</i> (K <sub>a</sub> '' = 7.7 × 10 <sup>-10</sup> ).					
0.004	0.0010	3.61	—	—	10.6 ± 0.7 × 10 <sup>4</sup>
0.010	0.0010	—	0.10	0.0712	5.9 ± 0.1 × 10 <sup>4</sup>
<i>m-Cresol</i> (K <sub>a</sub> '' = 0.98 × 10 <sup>-10</sup> ).					
0.002	0.0010	3.19	—	—	3.50 ± 0.18 × 10 <sup>5</sup>
0.002	0.0005	—	0.50	0.373	4.38 ± 0.03 × 10 <sup>5</sup>
<i>o-Nitrophenol</i> (K <sub>a</sub> '' = 7.5 × 10 <sup>-8</sup> ).					
0.004	0.0010	18.3	—	—	1.65 ± 0.13 × 10 <sup>3</sup>
0.010	0.0010	—	0.015	0.004	1.01 ± 0.02 × 10 <sup>3</sup>
<i>p-Nitrophenol</i> (K <sub>a</sub> '' = 9.6 × 10 <sup>-8</sup> ).					
0.010	0.0010	31.0	—	—	1.40 ± 0.10 × 10 <sup>3</sup>
0.010	0.0010	—	0.015	0.004	0.68 ± 0.03 × 10 <sup>3</sup>

The agreement between the velocity coefficients calculated over such exceptionally wide ranges of concentration is satisfactory and shows that the mechanism proposed is of general character; moreover, it eliminates the possibility of concurrent interaction of the hypochlorite ion with the phenoxide ion.

In order to differentiate between the two possible mechanisms of chlorination of a phenol by hypochlorous acid, the chlorination of salicylic acid has been studied. Here the alternative mechanisms become



In this case, unlike that of a simple phenol, the expression representing  $k_2/k_2'$  is not constant, but is inversely proportional to the hydroxyl-ion concentration. It is therefore possible, by examination of the speed of reaction in media of different hydroxyl-ion concentrations, to differentiate between the two theories, for on one mechanism only will velocity coefficients be obtained which are independent of the alkalinity of the medium.

The second ionisation constant of salicylic acid (Senter and Bulle, J., 1912, 101, 2532) is approximately  $1 \times 10^{-13}$ . In *N*/10-hydroxyl ion the disodium salt is 50% hydrolysed, and in *N*-hydroxyl ion 9% hydrolysed. If the interaction involves the hypochlorite ion, then the speed, on change of the alkalinity from *N*/10 to *N*, will be decreased 55 times,\* whilst if the phenoxide ion is involved the

\* The ratio of undissociated acid to monosodium salt is decreased 10 times and the monosodium salt concentration is decreased 5.5 times, giving a total decrease in the concentration of the undissociated acid of 55 times. The hypochlorite-ion concentration remains unaltered. The calculation is approximate, as the activities are not known.

corresponding decrease will be certainly less than 10 times (due to a 10-fold decrease in the un-ionised hypochlorous acid) since the concentration of the phenoxide ion has been increased 1.8 times, giving a net decrease of 5.5 times. Actually the observed decrease is 2.7 times, which is in favour of the phenoxide-ion theory.

TABLE V.

[Salicylic acid] = $10^{-2}$ ; [HOCl] = $10^{-3}$ ; $v = d[\text{OCl}^-]/dt$ (in mols./min.).						
[NaOH] = 0.10.			[NaOH] = 0.20.		[NaOH] = 1.00.	
[OCl <sup>-</sup> ] $\times 10^3$ .	<i>t</i> .	<i>v</i> $\times 10^5$ .	<i>t</i> .	<i>v</i> $\times 10^5$ .	<i>t</i> .	<i>v</i> $\times 10^5$ .
0.9	2.00	1.53	2.00	1.24	7.75	0.59
0.8	8.90	1.39	10.25	1.18	25.60	0.51
0.7	16.75	1.18	19.00	1.05	46.00	0.44
0.6	26.00	1.06	29.85	0.90	100.00	0.37

Further confirmation of the theory that the reaction involves the phenoxide ion is obtained from the behaviour in the initial stages of the reaction. The phenomenon is particularly clearly defined with *p*-nitrophenol, but is of general occurrence. If sodium hypochlorite is mixed with the phenol, the reaction proceeds smoothly without initial disturbance. If, however, sodium phenoxide be mixed with hypochlorous acid, as much as 35% of the hypochlorous acid may disappear before a portion of the solution can be removed for titration. The reaction after the initial disturbance is normal. The initial fall of titre in the one case is obviously due to the high concentrations of hypochlorous acid and phenoxide ion. An example of this effect is given in Table VI.

TABLE VI.

HOCl ( $10^{-3}$ ) added to <i>p</i> -nitrophenol ( $10^{-2}$ ) and NaOH ( $1.5 \times 10^{-2}$ ).		<i>p</i> -Nitrophenol ( $10^{-2}$ ) added to HOCl ( $10^{-3}$ ) and NaOH ( $1.5 \times 10^{-2}$ ).	
Time.	[OCl <sup>-</sup> ] $\times 10^4$ .	Time.	[OCl <sup>-</sup> ] $\times 10^4$ .
0	10	0	10
0.93	6.44	0.93	9.74
4.97	6.29	4.63	9.60
12.00	6.17	27.97	9.11

## 2. Chlorination of Phenols and Phenolic Ethers by Chlorine.

The presence of small traces of hydrochloric acid has a great effect on the speed of interaction of hypochlorous acid and a phenol. The speed is independent of the concentration and nature of the phenol, and is dependent on the hypochlorous acid concentration and the square of the hydrochloric acid concentration, thus:

$$v = k_1[\text{H}^+][\text{Cl}^-][\text{HOCl}] = k_1[\text{HCl}]^2[\text{HOCl}] \quad (5)$$

It is obvious that the speed measured is that of the formation of chlorine from hydrochloric and hypochlorous acids,\* the chlorine immediately reacting with the phenolic substance present. Using *p*-nitrophenol, a slower speed is observed, but on increasing its concentration the same limiting speed is obtained. Chlorine, therefore, chlorinates a phenol more rapidly than does hypochlorous acid. Some of the observed results obtained at 25.0° are in Table VII.

TABLE VII.

[HCl] =  $2 \times 10^{-4}$ ; [HOCl] =  $10^{-3}$ .

Substance.	<i>p</i> -Cresol.	Phenol.	Phenetole.	Anisole.	<i>p</i> -Nitrophenol.
Conc. to give limiting speed .....	$< 2 \times 10^{-3}$	$< 2 \times 10^{-3}$	$4 \times 10^{-3}$	$10^{-2}$	$10^{-2}$
$k \times 10^{-3}$ .....	2.17	2.14	2.16	2.14	2.06

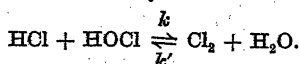
The velocity coefficient is unimolecular, since the concentration of the hydrochloric acid is constant, each molecule of chlorine which reacts with the phenol giving one molecule of hydrochloric acid, which in turn forms chlorine.

### 3. The Action of Hypochlorous Acid on Phenolic Ethers.

In dilute alkali, in which the existence of chlorine is excluded, no fall in titre of the mixture of ether and hypochlorous acid is observed. In water, however, a slow reaction occurs, the rate of which is only slightly dependent on the concentration of the ether present, and is thus probably due to chlorine. It is concluded that there is no detectable interaction between hypochlorous acid and the ether. By purification of the hypochlorous acid, as described in the experimental section, it was found that only a 2% loss of titre in 4 hours was experienced in a mixture of aqueous anisic acid and hypochlorous acid at 25°. This behaviour supports the theory that hypochlorous acid reacts with the phenoxide ion. Anisole, phenetole, and anisic acid cannot form the phenoxide ion, and therefore do not react.

The behaviour of chlorine is significant. It can chlorinate the ether as well as the phenol, so that the chlorination of phenolic

\* This velocity of formation of chlorine allows of the calculation of the speed of hydrolysis of chlorine, which is generally regarded as extremely rapid: The hydrolysis constant  $[\text{HOCl}][\text{H}^+][\text{Cl}^-]/[\text{Cl}_2]$  is  $4.84 \times 10^{-4}$  (Jakowkin, *loc. cit.*), and equals the ratio of the velocity coefficient of hydrolysis ( $k'$ ) to that of formation of chlorine by the reversible reaction ( $k$ )



Thus  $k'/k = 4.84 \times 10^{-4}$ , whence  $k' = 1.06 \times 10^{-3}$ . The speed of hydrolysis of chlorine is therefore relatively slow.

substances does not necessarily involve the phenoxide ion. This does not exclude the possibility of reaction between chlorine and the phenoxide ion in a solution of a phenol.

#### 4. Reactivity and Constitution.

The velocity coefficients of chlorination by hypochlorite of a number of phenols have been measured at 25.0°, chiefly in alkaline solution because control of the hydroxyl-ion concentration is facilitated. The results are in Table VIII.

TABLE VIII.

	$k_2$ .	$K_a''$ .	$k_2 K_a''$ .
Phenol .....	$3.3 \times 10^5$	$1.1 \times 10^{-10}$	$3.63 \times 10^{-5}$
o-Cresol .....	$1.25 \times 10^6$	$0.63 \times 10^{-10}$	$7.88 \times 10^{-5}$
m-Cresol .....	$4.4 \times 10^6$	$0.98 \times 10^{-10}$	$42.00 \times 10^{-5}$
p-Cresol .....	$9.0 \times 10^5$	$0.67 \times 10^{-10}$	$6.0 \times 10^{-5}$
o-Chlorophenol .....	$5.9 \times 10^4$	$7.7 \times 10^{-10}$	$4.55 \times 10^{-5}$
p-Chlorophenol .....	$4.90 \times 10^4$	$4.1 \times 10^{-10}$	$2.0 \times 10^{-5}$
3-Chloro-p-cresol .....	$1.67 \times 10^5$		
o-Nitrophenol .....	$1.01 \times 10^3$	$7.5 \times 10^{-8}$	$7.58 \times 10^{-5}$
m-Nitrophenol .....	$5.89 \times 10^3$	$1.0 \times 10^{-8}$	$5.89 \times 10^{-5}$
p-Nitrophenol .....	$6.84 \times 10^3$	$9.6 \times 10^{-8}$	$6.57 \times 10^{-5}$
1:3:4-Xylenol .....	$2.02 \times 10^6$		

The velocity coefficients differ considerably from one another, but the products of the velocity coefficient and the ionisation constant of the phenols are grouped in a noteworthy manner about the value  $7 \times 10^{-5}$ . It appears that the reactivity of the phenoxide ion is proportional to its affinity for hydrogen ion. Those ions derived from phenols of high ionisation constant are least reactive. These results may be compared with those of Boyd and Thomas (J., 1919, 115, 1239), who found a similar relation between the rates of interaction of phenoxide ions with olefine oxides.

#### 5. Discussion.

1. Since the speed of interaction of a phenol and hypochlorous acid is proportional to the product of the concentrations of the un-ionised acid and the phenoxide ion, the halogenating agent cannot be the positive halogen ion, for its concentration is proportional to the hypohalous acid concentration divided by that of the hydroxyl ion, *i.e.*,  $[Cl^+] = K[HOCl]/[OH^-]$ . The idea must also be abandoned in the case of chlorine, as its speed of chlorinating acetanilide, for example (Orton and King, J., 1911, 109, 1369), is independent of the excess of chlorine ions present. It appears that the molecules of chlorine or of hypochlorous acid react as whole molecules, and that therefore an intermediate complex must exist as a transient stage of the reaction.

2. It is probable that the theory of the reactivity of the phenoxide ion which has been proved for the interaction of hypochlorous acid and phenols also applies to the similar reactions involving hypobromous and hypoiodous acids. The conclusion of Vortmann (*Ber.*, 1923, 56, 234) that the alkali hypoiodite is the effective iodinating agent is based on evidence which also supports the mechanism involving the phenoxide ion. We find that the speed of iodination is decreased in strong alkaline solution, which can be explained by the great decrease in the concentration of the un-ionised hypoiodous acid.

3. Hypochlorous acid does not react with phenolic ethers, since they do not form the phenoxide ion, but chlorine interacts easily with both phenols and ethers. It is probable, however, that the interaction of chlorine with the phenol involves both the highly reactive phenoxide ion and the un-ionised phenol. Any alteration in the degree of ionisation of the phenol might be expected to alter the proportions of the isomeric products formed. Thus Arnall (*J.*, 1924, 125, 811) found that the proportions of *o*-, *m*-, and *p*-nitrophenols formed on nitration varied with the concentration of nitric acid present. This observation is consistent with the present theory of the reactivity of the phenoxide ion, the concentration of which varies with the acidity of the medium. The slower speed of bromination by bromine water in strong acid solution attributed by Francis (*loc. cit.*) to a decrease in the concentration of "nascent" bromine is also naturally explained on the present theory by the decrease in concentration of the phenoxide ion, the bromination of which is probably faster than that of the un-ionised molecule.

#### EXPERIMENTAL.

*Method of Titration.*—The course of a reaction was followed by estimation of the iodine liberated by the hypochlorous acid from acidified potassium iodide. The titration of iodine in the presence of a phenol must be carried out in acid solution in order to prevent interaction of the iodine and phenol. The consequent presence of free hydriodic acid, which is easily oxidised, is a source of error in the titration. The difficulty was overcome by using oxygen-free solutions and carrying out the titration in an atmosphere of nitrogen (compare Soper, *J.*, 1924, 125, 1899). Perfectly sharp end-points, with *N*/500-thiosulphate, were obtained in this way, even in the presence of 3*N*-sulphuric acid.

*Preparation and Purification of Hypochlorous Acid.*—The hypochlorous acid was prepared by passing chlorine into water containing yellow mercuric oxide in suspension, or by distillation of a



bleaching powder solution through which carbon dioxide was passed. Both specimens of hypochlorous acid behaved in the same way after purification. Two methods of purification were used: (a) repeated distillation of the hypochlorous acid from yellow mercuric oxide under reduced pressure; (b) simply shaking the hypochlorous acid with yellow mercuric oxide and after some time filtering off the oxychloride. The latter method was the one finally adopted, since the distillation method gave a hypochlorous acid which, on addition of sulphuric acid, formed traces of chlorine, the presence of which was manifested by the greater rate of reaction with phenol.

*Purity of Phenols.*—Kahlbaum specimens were purified either by several crystallisations from suitable solvents or by distillation, preferably under reduced pressure. Two distillations were usually found sufficient to give a pure phenol, the reactivity of which was unaltered by further distillation.

*Water.*—A high grade of conductivity water was used throughout. In such water a sample of hypochlorous acid showed no fall of titre in 60 hours.

#### *Summary.*

1. The interaction of phenols with hypochlorous acid in aqueous and in alkaline solution has been shown to involve the phenoxide ion and the un-ionised hypochlorous acid.

2. The reactivity of the ion with hypochlorous acid is least when the phenol from which it is derived is most strongly acidic. The reactivity of the ions of the simple phenols is roughly proportional to their affinity for hydrogen ions.

3. The chlorination of phenols and phenolic ethers by chlorine is a much faster reaction than the rate of formation of chlorine from a mixture of hydrochloric and hypochlorous acids, the velocity coefficient of which is  $2.2 \times 10^6$  at  $25^\circ$ . The calculated velocity coefficient of the hydrolysis of chlorine at this temperature is  $1.06 \times 10^3$ .

4. The mechanism of halogenation of phenols is discussed.

In conclusion, we wish to acknowledge the helpful criticism of Professor K. J. P. Orton, F.R.S.

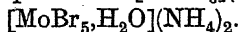
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CCVII.—*Compounds of Tervalent Molybdenum. Part IV. Bromides.*

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By electrolytic reduction of molybdenum trioxide dissolved in hydrochloric acid, solutions of tervalent molybdenum are obtained which, on addition of alkali chlorides, yield complex salts of the types  $[\text{MoCl}_6]\text{R}_3$  and  $[\text{MoCl}_5, \text{H}_2\text{O}]\text{R}_3$ . Although the trichloride has not yet been isolated from such solutions, when the concentration of molybdenum is high, the oxychloride,  $\text{MoOCl}_4 \cdot 4\text{H}_2\text{O}$ , can be obtained (J., 1924, 125, 2370). From the reduced bromide solutions, Rosenheim and Braun (*Z. anorg. Chem.*, 1905, 46, 311) have prepared two complex salts  $[\text{MoBr}_6](\text{C}_5\text{H}_5\text{N})_3$  and



In all these cases, the co-ordination number is 6. Moreover, the different halogen complexes containing molybdenum in other stages of oxidation exhibit this co-ordination number, for in such compounds an oxygen atom occupies only one co-ordination position: *e.g.*,  $[\text{MoO}_2\text{Cl}_4]\text{R}_2$ ,  $[\text{MoO}_2\text{Br}_4](\text{C}_5\text{H}_5\text{N})_3$ ,  $[\text{MoOX}_5]\text{R}_2$  where  $\text{X} = \text{Cl}, \text{Br}, \text{or F}$ .

On the Bohr theory of atomic structure, molybdenum, like chromium, iron, cobalt, nickel, rhodium, osmium and platinum, which all form well-defined compounds of co-ordination number 6, is a member of one of the groups of elements the planetary electrons of which are undergoing reorganisation. It shows, therefore, variable valency and marked colour in its compounds. The *maximum* co-ordination number of molybdenum is not, however, 6. A co-ordination number of 8 is seen in the complex salt  $\text{R}_4\text{Mo}(\text{CN})_8$ . This is in accordance with Sidgwick's rule that the maximum co-valency number or co-ordination number is that of the maximum sub-group next to the largest completed group in the atom. Molybdenum, atomic number 42, has its 3-quanta orbits completed and the numbers of electrons in the 4-quanta sub-groups are 2, 2, 4, 4, 6, 6, 8. So far, 6 represents the maximum co-ordination number for tervalent molybdenum and further evidence for this is afforded by the results of the present investigation, whereby, from a reduced solution of molybdenum trioxide in hydrobromic acid, a fawn-coloured oxybromide  $[\text{MoOBr}_4 \cdot 4\text{H}_2\text{O}]$  and red salts of the general formulæ  $\text{R}_3[\text{MoBr}_6]$  and  $\text{R}_2[\text{MoBr}_5, \text{H}_2\text{O}]$  have been isolated.

## EXPERIMENTAL.

*Molybdenyl Monobromide.*—The most satisfactory method for the preparation of constant-boiling hydrobromic acid is that outlined

by Scott (J., 1900, 77, 648), in which bromine is covered with water and reduced by sulphur dioxide and the resulting homogeneous liquid is distilled, the fraction boiling at 124—126° being collected and re-distilled.

In preparing his electrolyte, Rosenheim (*loc. cit.*) dissolved the dihydrate of molybdenum trioxide in the hydrobromic acid. However, the trioxide itself will dissolve in the hot acid. 25 G. of molybdenum trioxide and 350 c.c. of the hydrobromic acid were heated under reflux for 3 to 6 hours, the final solution being golden-brown in colour. The filtered solution was electrolysed in a diaphragm cell with smooth platinum electrodes (J., 1923, 123, 169), a current of 3.5 amps. being used, until the cathode solution was reddish-brown. This solution was transferred to an air-free flask and concentrated at 70° under diminished pressure to 80—100 c.c. The liquid was then transferred to a small cell and re-electrolysed to ensure that the molybdenum was tervalent. The electrolysis was continued until a sample of the liquid added to air-free acetone gave a flocculent fawn precipitate of molybdenyl bromide. (If the electrolysis is continued beyond this stage, the product is hydrolysed and much darker than the true compound.) The cathode solution was now forced by pressure of carbon dioxide into air-free acetone, and the solid which separated was filtered off and washed with acetone. All these operations were performed in an atmosphere of carbon dioxide, air being rigidly excluded. The solid was transferred to a desiccator which was then evacuated.

*Valency of the Compound.*—This was determined as for the oxychloride (*loc. cit.*). Direct titration with standard permanganate required, for 1 g. of solid, 118.90 c.c. After oxidation and passage through the reductor a solution containing 1 g. of the substance required 118.40 c.c. The molybdenum is therefore tervalent, for the latter titration represents the oxidation of the tervalent molybdenum, produced by reduction, to the sexavalent condition.

*Analysis.*—The molybdenum was precipitated as sulphide and ignited to trioxide (J., 1924, 125, 1911). The bromide in the filtrate and washings was weighed as silver bromide (Found: Mo, 37.5, 37.7; Br, 31.1, 31.3; Mo:Br = 1:1; 1:1.  $\text{MoOBr}_3 \cdot 5\text{H}_2\text{O}$  requires Mo, 37.7; Br, 31.35%). In all probability the normal hydrate is  $\text{MoOBr}_3 \cdot 4\text{H}_2\text{O}$ .

#### *Properties and Reactions of Molybdenyl Monobromide.*

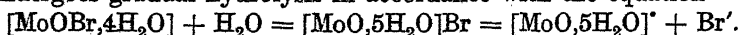
The dried solid is light fawn in colour and does not deliquesce in the air, although it gradually undergoes atmospheric oxidation. It is readily soluble in water or hydrobromic acid, its solubility in water being greater than that of the oxychloride. It is insoluble

in acetone or dry ether, slightly soluble in cold absolute alcohol and more soluble on warming. The substance has pronounced reducing properties. Silver nitrate is reduced to the metal, whilst with lead acetate acidified with acetic acid no precipitate of lead bromide is obtained. This test seems to indicate that molybdenyl bromide is not a binary electrolyte.

*Molecular Weight Determinations.*—The molecular weight was determined by depression of the freezing point of air-free water.

G. of $\text{MoOBr}_4 \cdot 4\text{H}_2\text{O}$ per 10 g. of water ...	0.1235	0.0640	0.0698
" Apparent " mol. wt. ....	218.8	218.2	220.1

If the salt has the formula  $[\text{MoOBr}_4 \cdot 4\text{H}_2\text{O}]$ , the molecular weight is 263.9, whereas if it is formulated as  $[\text{MoO}]\text{Br}_4 \cdot 4\text{H}_2\text{O}$  in dilute aqueous solution, if ionisation is complete, its "apparent" molecular weight should be 131.9. The above results furnish strong evidence in favour of its formulation as the co-ordination compound  $[\text{MoOBr}_4 \cdot 4\text{H}_2\text{O}]$ , although they also indicate that the substance undergoes gradual hydrolysis in accordance with the equation



This view receives support from the fact that the molecular weights determined with solutions of the solid, after standing some hours in ice-cold water, were considerably less than those quoted above, whilst after longer periods the hydroxide of molybdenum gradually separated.

Conductivity measurements at  $1^\circ$  showed this continuous hydrolysis, which was accelerated by the presence of the electrodes (compare Duff, J., 1923, 123, 572). For  $v = 24$  litres per mole

$\mu$ .....	66.8	68.2	75.2	76.1	76.9	77.6	77.8	78.2	78.2
Time (mins.) ...	2	3	4	5	6	7	8	9	10

In more dilute solutions, the rate of hydrolysis was increased. The fact that the conductivity alters with time and that it approaches the value for a binary electrolyte like potassium chloride, for which the data at  $1^\circ$  are

$v$ (litres per mole) .....	8	16	32
$\mu$ .....	72.2	75.2	77.3

supports the formula  $[\text{MoOBr}_4 \cdot 4\text{H}_2\text{O}]$  for the new compound. Many cases could be cited to show that ionisation of co-ordination compounds occurs with replacement of the co-ordinated halogen atom by a molecule of the solvent.

#### *Salts of the Types $\text{R}_3[\text{MoBr}_6]$ and $\text{R}_2[\text{MoBr}_5 \cdot \text{H}_2\text{O}]$ .*

By the addition of alkali bromide to a reduced bromide solution containing tervalent molybdenum, two salts have so far been pre-

pared conforming to the above types. The isolation of the oxy-bromide from a reduced molybdenum solution shows that a further possibility of complex salt formation may arise, namely, salts of the type  $\text{MoOBr}_x\text{KBr}$ . Although such a salt has not been isolated, the corresponding chlorine derivative  $[\text{MoOCl}_2\cdot 3\text{H}_2\text{O}]\text{K}$  has been obtained (unpublished research). The preparation of these three classes of salts depends on the following factors: (a) Molybdenum concentration, (b) relative amount of alkali bromide present, (c) amount of "free" acid. By suitable adjustment of these factors we have isolated  $\text{K}_3\text{MoBr}_8$ ,  $\text{K}_2\text{MoBr}_5$ ,  $\text{Cs}_2\text{MoBr}_5\cdot\text{H}_2\text{O}$ , and an impure rubidium salt of the last type.

*Preparation of Tripotassium Molybdenum Hexabromide.*—200 C.c. of the bromide solution containing tervalent molybdenum, to which was added a saturated aqueous solution of 10 g. of potassium bromide, were concentrated at  $65\text{--}70^\circ$  under diminished pressure to about 100 c.c. Air-free alcohol was then admitted to the flask, and the excess of potassium bromide precipitated. After filtration in an atmosphere of carbon dioxide, the filtrate was concentrated to 40 c.c. On addition of absolute alcohol a crystalline, light red solid was obtained which was filtered off and dried (Found: Mo, 13.9; Br, 69.0; K, 16.9.  $\text{K}_3\text{MoBr}_8$  requires Mo, 13.9; Br, 69.2; K, 16.9%). A valency determination showed the molybdenum in this salt to be tervalent.

*Preparation of Dipotassium Molybdenum Pentabromide.*—100 C.c. of the solution containing tervalent molybdenum and 20 c.c. of potassium bromide solution (containing 1.5 g.) were placed in an air-free flask and concentrated at  $65\text{--}70^\circ$  under diminished pressure until nearly dry. At this stage, air-free alcohol was admitted and a crystalline, brick-red salt separated which, after filtration and drying in an evacuated desiccator, was shown to contain tervalent molybdenum (Found: Mo, 16.7; Br, 69.5; K, 13.8.  $\text{K}_2\text{MoBr}_5$  requires Mo, 16.7; Br, 69.6; K, 13.6%).

This salt is obviously of the same type as the ammonium salt first obtained by Rosenheim and Braun (*loc. cit.*) and later by Foerster and Fricke (*Z. angew. Chem.*, 1921, 36, 2, 458). The former investigators formulated the dark garnet-red crystals as  $(\text{NH}_4)_2\text{MoBr}_5\cdot 2\text{H}_2\text{O}$ , whilst Foerster and Fricke considered them to be  $(\text{NH}_4)_2[\text{MoBr}_5\cdot\text{H}_2\text{O}]$ . By double decomposition with caesium bromide a solution of the potassium salt yielded the very insoluble  $\text{Cs}_2\text{MoBr}_5\cdot\text{H}_2\text{O}$  (Found: Mo, 12.3; Mo:Br = 1:5. Calc.: Mo, 12.3%).

A rubidium salt was prepared by a similar method to that used for the potassium derivative, but it could not be obtained pure.

*Properties of the Complex Salts.*

All these soluble complex salts give deep red solutions with water, in which both potassium salts are very soluble, the rubidium salt is sparingly soluble, and the caesium compound insoluble. The aqueous solutions gradually turn brown, then turbid, and finally yield a dark brown precipitate. This decomposition is accelerated by warming. The salts reduce copper sulphate solution to cuprous bromide, whilst silver nitrate solution is reduced to the metal.

The authors desire to thank Messrs. Brunner Mond and Co. for a grant in aid of this investigation and Professor G. T. Morgan, F.R.S., for his continuous interest.

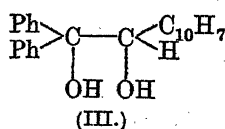
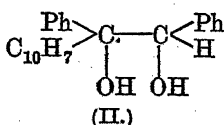
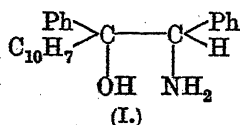
UNIVERSITY OF BIRMINGHAM,  
EDGBASTON.

[Received, April 24th, 1926.]

### CCVIII.—*The Dehydration of Glycols derived from $\alpha$ -Naphthylglycollic Acid.*

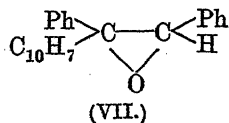
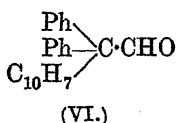
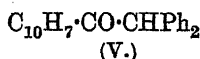
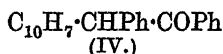
By ALEX. MCKENZIE and WALTER SAMUEL DENNLER.

THE present investigation arose from previous work on the deamination of 2-hydroxy-1 : 2-diphenyl-2- $\alpha$ -naphthylethylamine (I) and on the dehydration of  $\alpha$ -naphthylhydrobenzoin (II) (McKenzie and Richardson, J., 1923, 123, 79; McKenzie and Roger, J., 1924, 125, 844; McKenzie and Dennler, *ibid.*, p. 2105; Tiffeneau and Orékhov, *Compt. rend.*, 1924, 178, 1619). It appeared likely that 1- $\alpha$ -naphthyl-2 : 2-diphenylethylene glycol (III), which is isomeric with (II), would behave very differently when acted on by sulphuric acid. By arrangement with Professor Tiffeneau, it is now shown in the present paper that this is the case.

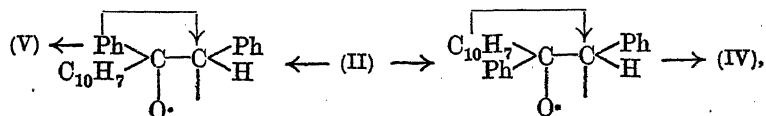


The products resulting from the elimination of water from (II) have already been shown to depend on the experimental conditions. With cold concentrated sulphuric acid, both  $\alpha$ -naphthyldeoxybenzoin (IV) and diphenylacetoneaphthone (V) were formed, whereas with hot dilute sulphuric acid the products were  $\alpha$ -naphthyldeoxybenzoin

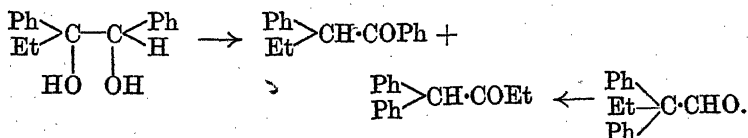
(IV), diphenyl- $\alpha$ -naphthylacetaldehyde (VI), and diphenyl- $\alpha$ -naphthylethylene oxide (VII).



Whilst the formation of both (IV) and (V) from (II) may be interpreted on the basis of semipinacolonic transposition,



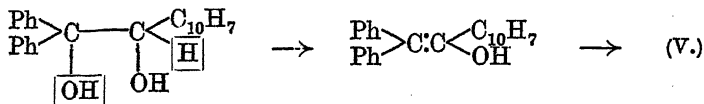
it should be noted that Danilov (*J. Russ. Phys. Chem. Soc.*, 1919, 51, 97) has shown that triphenylacetaldehyde undergoes molecular rearrangement into phenyldeoxybenzoin even under the influence of hot dilute sulphuric acid, thus:  $\text{CPh}_3\cdot\text{CHO} \rightarrow \text{CHPh}_2\cdot\text{COPh}$ . Similarly, Orékhov and Tiffeneau (*Compt. rend.*, 1926, 182, 67) have shown that substituted acetaldehydes undergo transformation into the same ketones as are formed by the direct dehydration of the corresponding glycols, e.g., a mixture of ethyldeoxybenzoin and diphenylbutanone is obtained either from diphenylethylacetaldehyde or from ethylhydrobenzoin:



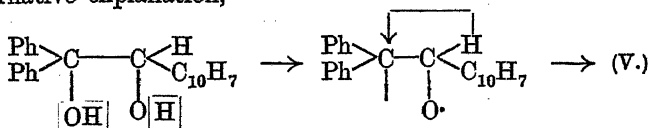
In the light of these results, it would appear quite probable that, in the formation of (IV) and (V) from (II), the intermediate product might be (VI). The proportion of (IV) and (V) in the mixture resulting from the dehydration of (II) with cold concentrated sulphuric acid varies according to the experimental conditions, and it might not be easy to arrive at this proportion experimentally, more particularly since the ketones melt at practically the same temperature. The recent work of Luce (*Compt. rend.*, 1925, 180, 145), however, would indicate that the migrational aptitude of  $\alpha$ -naphthyl is greater than that of phenyl, and one would argue that, in the mixture of ketones referred to, (IV) should preponderate.

1- $\alpha$ -Naphthyl-2:2-diphenylethylene glycol was prepared by the action of magnesium phenyl bromide on methyl  $\alpha$ -naphthylglycolate. It gave the same ketone, namely, diphenylacetone naphthone (V), irrespective as to whether cold concentrated sulphuric acid or hot

dilute sulphuric acid was used as the dehydrating agent, and its behaviour is thus quite different from that of the isomeric glycol (II). The change, which is best depicted as a vinyl dehydration, involves no transposition of phenyl:



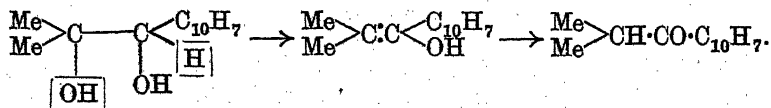
Since phenyl has undoubtedly a stronger saturation capacity than  $\alpha$ -naphthyl, the sum of the saturation capacities of the two phenyls will be greater than that of  $\alpha$ -naphthyl plus hydrogen. The alternative explanation,



which involves migration of hydrogen in preference to  $\alpha$ -naphthyl, is regarded as unsatisfactory.

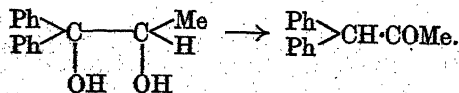
The researches of both Meerwein and Tiffeneau have demonstrated that phenyl has a strong saturation capacity, and a comparison of the results obtained by dehydrating (II) and (III) will show that the saturation capacity of phenyl is greater than that of  $\alpha$ -naphthyl. Obviously, the dehydration of (III) is not a semipinacolinic change; if it were, the product would be (IV) and not (V). Of the two hydroxyls, the tertiary is the more loosely bound, because the saturation capacity of the two phenyl groups more than balances the saturation capacity of  $\alpha$ -naphthyl plus hydrogen.

1- $\alpha$ -Naphthyl-2:2-dimethylethylene glycol was prepared from methyl  $\alpha$ -naphthylglycolate and magnesium methyl iodide. Its behaviour on dehydration is similar to that of (III):



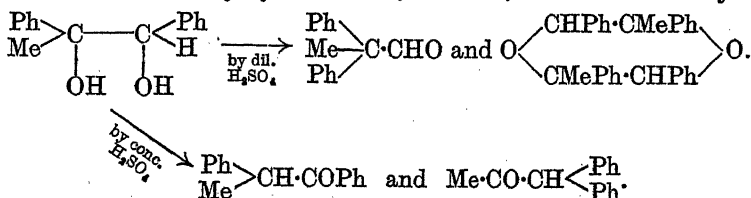
This result was anticipated, since methyl has a strong saturation capacity.

The behaviour of (III) and (II) on dehydration has a parallel in two other cases which may be quoted. Thus, diphenylpropylene glycol gives diphenylacetone both with hot dilute and with cold concentrated sulphuric acid:



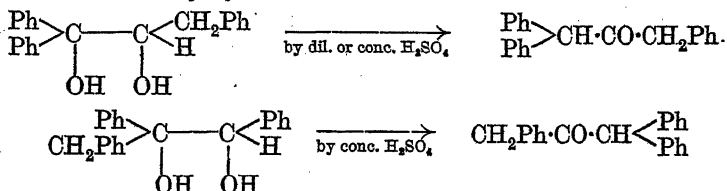


The isomeric methylhydrobenzoin, however, behaves differently :



(For literature, see McKenzie and Roger, *loc. cit.*)

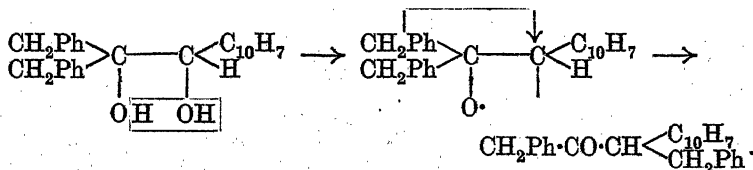
Again, *as*-benzylidiphenylethylene glycol may be contrasted with the isomeric benzylhydrobenzoin :



(Orékhov, *Bull. Soc. chim.*, 1919, **25**, 107).

Here the same ketone is produced by two different mechanisms, migration of phenyl taking place in the one case and not in the other.

The ketones formed from 1- $\alpha$ -naphthyl-2:2-diphenylethylene glycol and 1- $\alpha$ -naphthyl-2:2-dimethylethylene glycol, respectively, cannot exist in optically active modifications. To obtain such a ketone from a glycol derived from optically active  $\alpha$ -naphthylglycollic acid, it would be necessary for semipinacolinic change to occur during the dehydration of the glycol instead of the vinyl dehydration as in the two other cases, and even then optical activity might not persist. Accordingly, since Tiffeneau and Lévy (*Bull. Soc. chim.*, 1923, **33**, 759) have shown that benzyl has a greater migrational aptitude than methyl and also has a weaker saturation capacity, the examination of the dehydration of 1- $\alpha$ -naphthyl-2:2-dibenzylethylene glycol (VIII), prepared by the action of magnesium benzyl chloride on methyl  $\alpha$ -naphthylglycollate, was undertaken. The change is apparently semipinacolinic :



#### EXPERIMENTAL.

*Preparation of  $\alpha$ -Naphthylglycollic Acid.*—(1) From  $\alpha$ -naphthoic acid. Boessneck's method (*Ber.*, 1883, **16**, 639) was modified as

follows:  $\alpha$ -Naphthoic acid (40 g.)  $\rightarrow$  acid chloride (37 g.), b. p. 170—172°/15 mm.,  $\rightarrow$   $\alpha$ -naphthoyl cyanide (27 g.), m. p. 100°,  $\rightarrow$   $\alpha$ -naphthoylformamide (24 g.), m. p. 151—153°,  $\rightarrow$   $\alpha$ -naphthoylformic acid (15 g.), m. p. 110—111°. The latter acid was reduced by aluminium turnings and an excess of caustic potash, the excess of aluminium removed, and the hydroxy-acid obtained by acidification by hydrochloric acid and extraction with ether. It crystallised from benzene in rectangular needles, m. p. 80—82°, and was then dried in a vacuum. Yield: 14 g.; m. p. 98.5—99.5° (Found: C, 71.2; H, 5.0. Calc.: C, 71.3; H, 5.0%). Boessneck does not quote the melting point of his acid, but Brandis (*Ber.*, 1889, 22, 2148), who obtained the acid from  $\alpha$ -naphthaldehyde by the cyanohydrin method, gives m. p. 80—81°.

(2) *From naphthalene.*  $\alpha$ -Naphthyl methyl ketone (14 g.), prepared from naphthalene by the Friedel and Crafts reaction (Caille, *Compt. rend.*, 1911, 153, 393), was brominated (Schweitzer, *Ber.*, 1891, 24, 549). Caustic potash (25 g. in 250 c.c. of water) was added to the dibromide and, after a fortnight, the acid obtained by acidification and extraction with ether was crystallised from benzene (yield of dry acid, 5 g.; m. p. 98—99°. Schweitzer gives m. p. 91—93°).

(3) *From chloral* (compare Hébert, *Bull. Soc. chim.*, 1920, 27, 45). The Grignard reagent prepared from 150 g. of  $\alpha$ -bromonaphthalene (1 mol.) was cooled to -12°, and an ethereal solution of 98 g. of anhydrous chloral (1 mol.) gradually added (90 min.). The action was very vigorous, the ether assumed a blood-red tint, and a solid separated. The mixture remained at 0° over-night, and was then decomposed by ice and dilute acetic acid. The oil resulting from the ethereal solution was mixed with an excess of sodium carbonate, and, after hydrolysis of the trichloro-alcohol and removal of the naphthalene by steam, the aqueous solution was acidified by concentrated hydrochloric acid, and the hydroxy-acid extracted with ether (yield: 70 g.). The acid after crystallisation from benzene and drying in a vacuum melted at 98—99°. Its silver salt gave Ag, 35.0 (Calc.: Ag, 35.0%).

Of those three methods, the third was in our experience the most practicable.

$\alpha$ -Naphthylglycollic acid gives a blue coloration when a trace is added to cold concentrated sulphuric acid. Its methyl ester is sparingly soluble in light petroleum, from which it separates in needles, m. p. 79°, as given by Schweitzer (*loc. cit.*) (Found: C, 72.2; H, 5.6. Calc.: C, 72.2; H, 5.6%). When heated under pressure at 100° with aqueous ammonia ( $d$  0.88), the ester was converted into  $\alpha$ -naphthylglycollamide,  $C_{10}H_7\cdot CH(OH)\cdot CO\cdot NH_2$ , which crystallises

from acetone-light petroleum in rhombic plates, m. p. 134—135° (Found: C, 71.8; H, 5.7.  $C_{12}H_{11}O_2N$  requires C, 71.7; H, 5.5%). An attempt to prepare the ketol,  $C_{10}H_7\cdot CH(OH)\cdot CO\cdot C_6H_5$ , by the action of an excess of magnesium phenyl bromide on the acid amide led to the regeneration of the latter.

*Action of Grignard Reagents on Methyl  $\alpha$ -Naphthylglycollate.*

*Action of Magnesium Phenyl Bromide.*—An ethereal solution of 5 g. of the ester (1 mol.) was added during 45 minutes to the Grignard reagent prepared from 16 g. of bromobenzene ( $4\frac{1}{2}$  mols.). A solid separated during the heating (9 hours). The product was decomposed with ice and ammonium chloride and, after the usual manipulation, diphenyl was removed by light petroleum. The 1- $\alpha$ -naphthyl-2:2-diphenylethylene glycol (III) obtained crystallised from light petroleum (b. p. 60—100°), in which it was sparingly soluble, in rectangular needles, m. p. 126—127° (yield 6.1 g.). It gives a bright green coloration with concentrated sulphuric acid. For analysis, it was dried in a vacuum at 80° (Found: C, 84.6; H, 6.0.  $C_{24}H_{20}O_2$  requires C, 84.7; H, 5.9%).

*Action of Magnesium Methyl Iodide.*—The conditions were similar to the preceding (15 g. of the ester [1 mol.]; Grignard reagent prepared from 60 g. of methyl iodide [6 mols.]; decomposition with ice, ammonium chloride and ammonia). The crude product was crystallised twice from light petroleum, 1- $\alpha$ -naphthyl-2:2-dimethylethylene glycol,  $C_{10}H_7\cdot CH(OH)\cdot CMe_2\cdot OH$ , being obtained (11 g.) in clumps of rectangular prisms, m. p. 81.5—82° (Found: C, 78.0; H, 7.5.  $C_{14}H_{16}O_2$  requires C, 77.8; H, 7.5%). It gives a reddish-brown coloration with concentrated sulphuric acid.

*Action of Magnesium Benzyl Chloride.*—An ethereal solution of 14 g. of the ester (1 mol.) was added during 90 minutes to the Grignard reagent prepared from 40 g. of benzyl chloride ( $4\frac{1}{2}$  mols.). A solid separated during the heating (10 hours). The product was decomposed with ice and dilute sulphuric acid, and dibenzyl removed by light petroleum. The 1- $\alpha$ -naphthyl-2:2-dibenzylethylene glycol (VIII) obtained crystallised from rectified spirit in rectangular plates (17 g.), m. p. 174—175° (Found: C, 84.8; H, 6.7.  $C_{26}H_{24}O_2$  requires C, 84.8; H, 6.6%). It gives a purple coloration with concentrated sulphuric acid.

*Dehydration of Glycols derived from Methyl  $\alpha$ -Naphthylglycollate.*

*Dehydration of the Diphenyl Glycol.*—(a) *With concentrated sulphuric acid.* 2 G. of finely-powdered 1- $\alpha$ -naphthyl-2:2-diphenylethylene glycol were triturated in instalments with 30 c.c. of concentrated sulphuric acid during 2 hours. The bright green color-

ation which appeared at first changed gradually to a greenish-brown. The mixture was added to 100 g. of ice, and the ethereal extract dried with sodium sulphate. The resulting oil gradually solidified, and the solid crystallised from rectified spirit in glistening rhombic plates, m. p. 108—109°. The compound (0.9 g.) was identified as diphenylacetone naphthone by its colour reaction with concentrated sulphuric acid, and by the non-depression of melting point when mixed with a specimen of the ketone prepared by the dehydration of  $\alpha$ -naphthylhydrobenzoin with concentrated sulphuric acid (McKenzie and Roger, *loc. cit.*).

(b) *With dilute sulphuric acid.* A mixture of the glycol (2 g.), water (16 c.c.), and concentrated sulphuric acid (20 g.) was boiled for 2 hours under reflux. The mixture was cooled, diluted with water, and the oil extracted with ether. The product was crystallised from ethyl alcohol, and diphenylacetone naphthone (1.5 g.), identified as above, was isolated.

*Dehydration of the Dimethyl Glycol.*—(a) *With concentrated sulphuric acid.* 7 G. of 1- $\alpha$ -naphthyl-2:2-dimethylethylene glycol were dehydrated with 100 c.c. of concentrated sulphuric acid. 2 G. of a golden-yellow oil, b. p. 295—298°, were collected.

(b) *With dilute sulphuric acid.* 10 G. of the glycol were boiled for 2½ hours with a mixture of 100 g. of concentrated sulphuric acid and 100 c.c. of water. The resulting oil was fractionated, and the portion boiling at 304—306°/758 mm. was collected. It did not reduce Fehling's solution, nor did it restore the colour to Schiff's reagent. Yield 6 g. (Found: C, 85.3; H, 7.0. Calc. for  $C_{14}H_{14}O$ : C, 84.8; H, 7.1%). This was isopropyl  $\alpha$ -naphthyl ketone, which according to Rousset (*Bull. Soc. chim.*, 1896, 15, 66) has b. p. 308—310°. The scission of the oil with alcoholic potash gave a solution of potassium salt from which  $\alpha$ -naphthoic acid was isolated, and the oil from the dehydration with concentrated sulphuric acid underwent a similar decomposition.

*Dehydration of the Dibenzyl Glycol.*—(a) *With concentrated sulphuric acid.* 10 G. of 1- $\alpha$ -naphthyl-2:2-dibenzylethylene glycol were gradually added (1 hour) with constant trituration to 220 g. of concentrated sulphuric acid. A purple coloration was noted. After being kept for 2 hours at the ordinary temperature, the mixture was poured into 500 g. of ice; the purple coloration then disappeared and the temperature fell quickly to -2°. When the ice had melted, the oil was extracted with ether, the ether expelled, and the residue (7 g.) distilled under diminished pressure. The compound,  $C_{26}H_{22}O$ , was a golden-yellow oil, b. p. 275°/15 mm. For analysis, it was dried in a vacuum (Found: C, 89.3; H, 6.3.  $C_{26}H_{22}O$  requires C, 89.2; H, 6.2%). It solidified after several days,

and was then crystallised from rectified spirit, from which it separated in rhombic plates, m. p. 58—59°. With concentrated sulphuric acid, it gave a light brown coloration which disappeared quickly.

(b) *With dilute sulphuric acid.* A mixture of the glycol (15 g.), water (125 c.c.), and concentrated sulphuric acid (120 g.) was boiled for about 2½ hours under reflux, and the oil extracted with ether. The product was an oil (13.5 g.), b. p. 276°/15 mm., which gradually solidified; m. p. 58—59°.

The substance is probably benzyl- $\alpha$ -naphthylmethyl benzyl ketone,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{C}_{10}\text{H}_7)\cdot\text{CH}_2\text{Ph}$ , but the evidence for its constitution is not quite convincing. It formed no oxime with hydroxylamine, and it is very stable towards alcoholic soda; thus, when 2.5 g. were heated at 100—140° for 24 hours with a solution of 6 g. of caustic soda in ethyl alcohol, the original substance was recovered. It gave, however, benzoic acid when it was oxidised in glacial acetic acid solution with chromic anhydride. The first product of the oxidation was presumably phenylacetic acid; it was found that the latter does give benzoic acid when oxidised under similar conditions to those adopted for the compound.

The thanks of the authors are due to the Department of Scientific and Industrial Research for a maintenance grant awarded to one of them (W. S. D.).

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

[Received, February 20th, 1926.]

## CCIX.—*The Complexity of the Solid State. Part IV. The Behaviour of Pure Sulphur Trioxide. Part III.*

By ANDREAS SMITS and PIETER SCHOENMAKER.

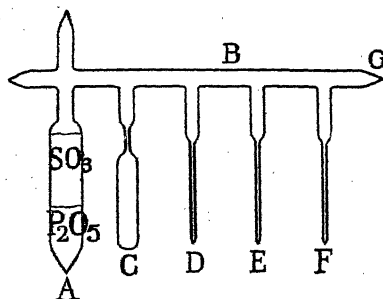
### *Investigations with X-Rays.*

As shown in our last publication (this vol., p. 1120), it is possible by partial distillation to obtain the intensively dried, high-melting, asbestos-like form in a condition having an abnormally low vapour pressure and an initial melting point which is 33° higher than the unary melting point. It appears, indeed, that this form of sulphur trioxide behaves as a mixed crystal; the most volatile pseudo-component can be distilled off, so that the residue is a substance having the above abnormal properties.\*

\* Only the states of aggregation of a single substance in inner equilibrium will be called "modifications"; the states not in inner equilibrium will be termed "forms" of the substance.

For the X-ray investigation of the different states of the high-melting, asbestos-like form we used the simple apparatus of high-melting Jena glass shown in Fig. 1. The bulb, A, is sealed to B along with a vessel, C, and three very thin-walled capillary tubes, D, E, and F (diameter 0.008 to 0.01 mm.). Bulb A is partly filled with freshly-distilled phosphorus pentoxide and then with intensively dried sulphur trioxide, as described in our first communication (J., 1924, 125, 2557). The apparatus is then evacuated and the tube

FIG. 1.



B is sealed off at G.

The capillary tubes were filled one after another with the high-melting, asbestos-like form by the method of condensation and evaporation. In order to obtain a form with an abnormally low vapour pressure, a part of the contents was distilled off rapidly and the capillaries were subsequently sealed off.

The Röntgenogram was then taken, using  $\text{CuK}_\alpha$ -rays. We obtained a film of 15 lines, the strongest of which are given in the following table:

Distances (mm.).....	8.9	11.6	13.2	16.4
$10^\circ \times \sin^2 \theta/2$ .....	32	54	70	106

( $\theta$  is the angle between the incident and refracted beams; the intensities of the lines mentioned here were very strong.)

The same capillary was now heated at  $50^\circ$  for 48 hours and, since our experiments had shown that under these conditions the low vapour pressure of the high-melting, asbestos-like form (which had been disturbed by evaporation) increased strongly, it was expected that the Röntgenogram taken after this heating process would show a great difference. *It was, however, unchanged. Hence, either the X-ray method was unable to detect the change which had taken place in the solid, or the X-rays had already effected the establishment of the inner equilibrium during the first exposure, so that the state of the solid before and after the heating was in reality the same.*

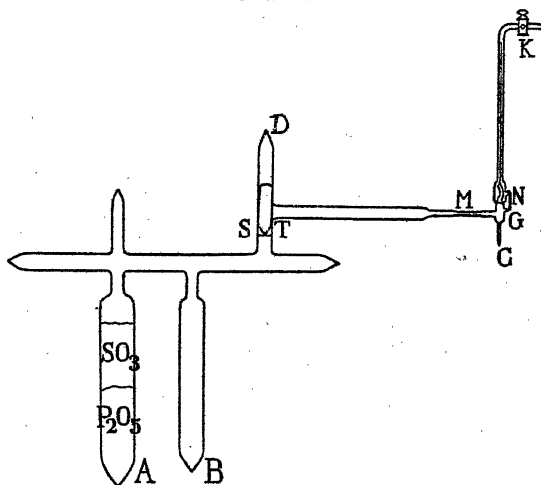
#### X-Rays effect the Establishment of the Inner Equilibrium.

To decide between the alternatives mentioned above, the following apparatus (Fig. 2) was constructed. As in other cases, pure phosphorus pentoxide was first distilled into vessel A, and then intensively dried sulphur trioxide. A T-piece with septum S was then connected with an exceedingly small glass spring indicator,

G, the little vessel of which was provided with a very thin-walled capillary, C, as used in X-ray analysis. The storage apparatus containing the sulphur trioxide was first evacuated and sealed; then the glass spring indicator with its capillary and the T-piece with its breaker were heated to redness in a current of dried air, the breaker-tube was sealed off at D, and this part of the apparatus was evacuated by stopcock K.

Capillary N being sealed off, a part of the sulphur trioxide was distilled into B and this vessel also was sealed off. Septum S was then broken and the capillary C filled with the high-melting, asbestos-like form, by the method of alternate condensation and evaporation.

FIG. 2.



In order to get a highly-disturbed state of this form, a portion was distilled off in the way described above, and then the capillary M was sealed off. The vapour pressure at the ordinary temperature was only 1 cm. Hg, proving that we had indeed a strongly-disturbed state of the high-melting, asbestos-like form.

We now placed the apparatus in front of our X-ray tube, protecting it by asbestos plates from access of heat. The X-rays were allowed to penetrate only the capillary containing the sulphur trioxide. As soon as this capillary was exposed to the X-rays the pressure in the indicator began to rise, showing that X-rays rapidly effect a transformation in the direction of inner equilibrium. In order to determine the final pressure, observations were continued over a period with the following results :

Time of exposure (hrs.) .....	0	1	4	8	10	13
Vapour pressure (mm. Hg) ...	10.8	22.2	43.1	46.1	46.3	46.3
Temperature .....	18.0°	18.0°	18.0°	18.8°	19.7°	19.7°

Consequently the final vapour pressure is 46.3 mm. Hg at 19.7°. As shown previously (this vol., p. 1116), the vapour-pressure line for the high-melting, asbestos-like form in inner equilibrium is given by the equation  $T \ln P = -Q/R + CT$ , where  $C = 32.0$ . Now, giving  $Q/R$  the mean, *i.e.*, 8243 cal., of the three values obtained (8246, 8236 and 8246 cal.), we find, for  $T = 292.7^\circ$  (*i.e.*, 19.7° C.),  $P = 46.45$  mm. Hg.

The agreement of this figure with the final value shown in the foregoing table proves that X-rays do indeed effect the establishment of inner equilibrium. It appears, therefore, that the X-ray diagrams showed no difference because, on exposure to X-rays, the substance was transformed into the state of inner equilibrium. This very interesting result shows that it is impossible to study the disturbed states of sulphur trioxide more closely by means of X-rays.

*X-Rays bring about the Transformation of the Metastable into the Stable Modification.*

Finally we investigated the X-ray diagrams of the two metastable modifications of sulphur trioxide—the ice-like form and the low-melting, asbestos-like form. Not only were the films obtained identical, but the X-ray diagram in each case was that of the high-melting, asbestos-like form considered above.

Hence X-rays, besides effecting the establishment of the inner equilibrium of sulphur trioxide, transform the metastable states into the stable state, *i.e.*, the high-melting, asbestos-like modification. *The only X-ray diagram obtainable is accordingly that of the stable modification in inner equilibrium.*

*Summary.*

On distillation of a portion of the intensively dried, high-melting, asbestos-like form, different states having abnormally low vapour pressures and abnormally high initial melting points were obtained, thus showing that the intensively dried, high-melting, asbestos-like form behaves as a mixture of pseudo-components which have very different vapour pressures and melting points.

At the ordinary temperature these states do not alter, but at 50° changes take place in the direction of the inner equilibrium. On studying the unchanged state and that changed at 50°, by means of X-rays, a very interesting result was obtained: the Röntgenograms in these two cases were identical.

Using an apparatus which enabled us to determine the vapour pressure during the exposure to X-rays, we found the explanation of the interesting phenomenon mentioned above to lie in the fact



that the X-rays effect a very rapid increase of the vapour pressure, proving that X-rays cause a rapid change in the direction of the inner equilibrium. Calculation showed that the final vapour pressure was exactly that of the high-melting, asbestos-like form in inner equilibrium.

X-Rays bring about not only the establishment of the inner equilibrium, but also the transformation of the metastable modifications into the stable form. The films obtained by exposing the ice-like form and the low-melting, asbestos-like form to X-rays are thus identical with the film of the high-melting, asbestos-like modification.

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### CCX.—*The Photolysis of Acetaldehyde and of Acetone.*

By EDMUND JOHN BOWEN and HAROLD GARFIT WATTS.

It was shown by Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 68, 233) that acetaldehyde is partly polymerised in ultra-violet light and partly decomposed into methane and carbon monoxide; also (*ibid.*, 1910, **151**, 478) that acetone is decomposed into ethane and carbon monoxide. In aqueous solutions acetone is said to be photolysed to methane and acetic acid.

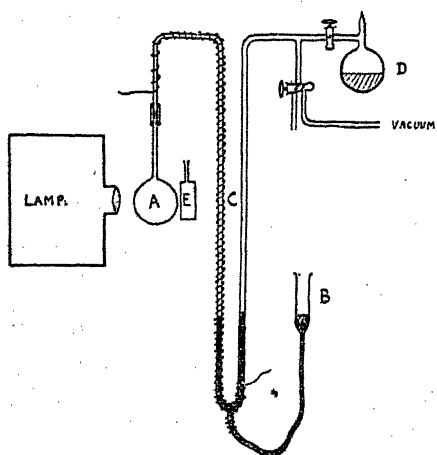
The following experiments were made to compare the number of molecules chemically changed with the number of molecules activated, *i.e.*, with the number of quanta absorbed. No work of this kind on gaseous aldehydes and ketones seems to have been done, although Volmar (*Compt. rend.*, 1924, **178**, 697), apparently without experimental evidence, assumed that these reactions obeyed the Einstein-Stark law.

#### *Experiments with Acetaldehyde Vapour.*

The apparatus is shown diagrammatically in the figure. A mercury vapour lamp made by the Thermal Syndicate was contained in a box fitted with quartz condensing lenses so that approximately parallel light fell on the fused quartz reaction bulb A, which was filled with acetaldehyde vapour by lowering the mercury reservoir B, evacuating with two mercury vapour pumps in series, and then connecting with the liquid aldehyde in D through the tap. The reservoir B was then raised so that mercury rose in the limbs of the U-tube C, and the tap on the right hand limb opened to the atmosphere. The amount of photochemical change was measured by pressure changes in the left hand limb, which was heated electrically to prevent condensation of liquid.

For the measurement of the energy of the ultra-violet light, use was made of the "ultra-violet radiometer" of Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, 47, 718) which is based upon the decomposition of oxalic acid in uranyl sulphate solutions. There is a serious discrepancy in the results of different investigators of this reaction. Anderson and Robinson state that in ultra-violet light 1 molecule of oxalic acid is decomposed for every 25 quanta absorbed; Boll (*Compt. rend.*, 1913, 156, 1891) states that 50 molecules of oxalic acid are decomposed for each quantum absorbed; whilst Büchi (*Z. physikal. Chem.*, 1924, 111, 269) finds that the reaction obeys the Einstein-Stark law. We therefore

FIG. 1.



made direct measurements of the photochemical efficiency of this reaction.

The mercury vapour lamp with quartz condensing lenses was set up with a 5 cm. water-filter, and the light passed through a stop on to a cell with fused-on ends of plane-polished quartz containing the uranyl sulphate (0.01*M*) and oxalic acid (0.1*N*) solutions. The oxalic acid decomposed was estimated with *N*/20-potassium permanganate solution, and

the total energy of the light measured with a Moll thermopile calibrated against a Hefner lamp (Gerlach, *Physikal. Z.*, 1913, 14, 577). The amount of light absorbed was obtained from the difference in readings of the galvanometer connected to the thermopile when the quartz cell contained water or the solution. The results were as follows :

Galvanometer readings (1 division =  $1.4 \times 10^{-4}$  cal./sec.) :

Total energy of lamp falling on cell = 50 divisions.

Quartz cell filled with water = 30.5 "

" " " " solution = 17.5 "

Thus, cal. absorbed by solution per sec. =  $2.8 \times 10^{-3}$ .

Taking the Hg line 3130 Å. as the mean wave-length absorbed, 1 gram-molecular quantum = 85,000 cal.; therefore the number of gram-molecular quanta absorbed per sec. =  $3.3 \times 10^{-8}$ . In these experiments, each of 1 hour's exposure, the amount of oxalic

acid decomposed per second was  $3.0$ ,  $3.35$ , and  $3.5 \times 10^{-8}$  g.-mol., respectively. From these results it appears that it may safely be assumed, in agreement with Büchi, that for each quantum of ultra-violet light absorbed one molecule of oxalic acid is decomposed.

The absorption of the aldehyde vapour was then measured by the difference in the photochemical change taking place in the uranyl sulphate-oxalic acid solution in the plane-walled quartz vessel E when the bulb A was empty and when it was filled with aldehyde vapour; also, by placing the vessel E in the place of A, the total amount of ultra-violet light could be measured.

Acetaldehyde undergoes two photochemical changes:

- (1) Photolysis,  $\text{CH}_3\cdot\text{CHO} = \text{CH}_4 + \text{CO}$ .
- (2) Polymerisation,  $3\text{CH}_3\cdot\text{CHO} = \text{paraldehyde} + \text{metaldehyde}$ , etc.

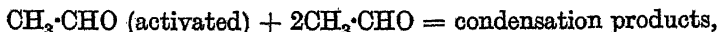
The first series of measurements was made with a little liquid aldehyde in the bulb, *i.e.*, with saturated vapour, only the vapour being exposed to the light. If  $x$  molecules are changed according to reaction (1), the pressure change will be proportional to  $2x$ , the second reaction giving condensation products which do not affect the pressure appreciably. The results were:

Volume of reaction vessel = 125 c.c.

Pressure *increases* in cm. Hg after 1 hour's exposure. =  $\begin{cases} 0.59, 0.665, 0.55, 0.685. \\ \text{Mean} = 0.62. \end{cases}$

Thus,  $2x = 125 \times 0.62/3600 \times 76 \times 23400 = 1.2 \times 10^{-8}$  g.-mol./sec. or  $x = 0.6 \times 10^{-8}$  g.-mol./sec.

A second series of experiments was made with unsaturated vapour; a diminution in pressure then took place showing that more molecules are polymerised than photolysed. If  $y$  is the number of molecules activated for the reaction



the diminution in pressure is proportional to  $(3y - x)$ . The results were:

Pressure *decreases* in cm. Hg. after 1 hour's exposure. =  $\begin{cases} 3.5, 3.9, 3.3, 3.8, 2.8, 2.4. \\ \text{Mean } 3.5. \end{cases}$

Thus,  $3y - x = 125 \times 3.5/3600 \times 76 \times 23400 = 6.85 \times 10^{-8}$  g.-mol./sec., whence  $y = 2.48 \times 10^{-8}$  g.-mol./sec.

Total number of g.-mols. activated per second for photolysis and polymerisation =  $x + y = 3.08 \times 10^{-8}$ .

Number of gram-molecular quanta absorbed per second by aldehyde vapour (obtained from oxalic acid-uranyl sulphate solution titrations) =  $1.42 \times 10^{-8}$ .

Allowing for the inaccuracy of the measurements and the complexity of the decomposition products of acetaldehyde, the results indicate that two molecules are chemically activated for each quantum absorbed.

*Experiments with Acetone Vapour.*

The same apparatus was used except that an air-bath was placed round the reaction bulb to keep the acetone as an unsaturated vapour at about 750 mm. and 60°. The amount of light absorbed was taken to be equal to that measured in the experiments on aqueous solutions of acetone described below, as, the concentrations of acetone being equal, it has been shown that the extinction coefficients of gaseous and of dissolved acetone are not very different (Porter and Iddings, *J. Amer. Chem. Soc.*, 1926, 48, 40). The results were:

Vol. of bulb (c.c.).	Exposure (mins.).	Press. change (cm. Hg).	No. of g.-mols. acetone decomp. per sec.
125	245	2.42	$1.34 \times 10^{-8}$
80	160	3.63	} $1.81 \times 10^{-8}$ (mean)
80	135	3.35	

Number of gram-molecular quanta absorbed per sec. =  $1.0 \times 10^{-8}$ .

Other experiments were made at room temperature in an apparatus consisting of two bulbs filled with acetone vapour connected by a U-tube containing liquid acetone. The apparatus was immersed in a thermostat before and after exposing one bulb (of quartz) to the lamp, and the photochemical change determined by the change in level of the liquid in the U-tube. The energy in the light absorbed was directly measured with the oxalic acid-uranyl sulphate solution. The results were:

Exposure = 1 hour. Volume of bulb = 125 c.c.

Pressure change (cm. Hg) = 0.212, 0.176, 0.141, 0.159, 0.247.

Taking the average as 0.187 cm. Hg, the number of g.-mol. of acetone decomposed per second is  $2 \times 10^{-9}$ . The mean of several oxalic acid titrations gave the number of gram-molecular quanta per second =  $4.85 \times 10^{-9}$ . The number of molecules chemically changed is very close to the number of quanta absorbed.

The accuracy of these low-pressure measurements was not so great as that of the high-pressure ones, so that it is not certain whether the diminution in quantum sensitivity is real or due to experimental errors.

A further series of experiments was made with hot acetone vapour, oxalic acid-uranyl sulphate solutions being used to measure the absorption.

The results were: Volume of bulb = 125 c.c. Exposure = 60

minutes. Pressure change (cm. Hg.) = 0.60, 0.82, 0.815, 0.77, 0.71, 0.80, 0.60, 0.90.

Taking the mean as 0.75, the number of g.-mol. of acetone decomposed per second =  $1.5 \times 10^{-8}$ .

The mean of several oxalic acid titrations gave the number of gram-molecular quanta absorbed per second =  $0.867 \times 10^{-8}$ .

It seems that about two molecules of acetone are decomposed for each quantum absorbed.

*Experiments with Aqueous Solutions of Acetone.*

It is stated by Henri (*Compt. rend.*, 1913, 156, 1012) that about 1300 molecules of acetone are hydrolysed for each quantum of ultra-violet light absorbed. He appears to have used an open quartz cell to contain the solution, and must have lost acetone by evaporation. In our experiments, solutions of acetone were exposed in a closed plane-walled quartz cell to an approximately parallel beam of ultra-violet light, and the number of quanta absorbed measured with the oxalic acid-uranyl sulphate solution. When the acetone solution was titrated iodimetrically, the photochemical change was too small to be measurable, although if the reaction followed the Einstein-Stark law it should have been recognisable. The acetic acid formed was therefore estimated with very dilute baryta solution, and the following mean results were obtained :

Conc. of acetone solution %.	G.-mols. acetic acid formed per sec.	G.-molecular quanta absorbed per sec.
0.3	$5.7 \times 10^{-10}$	$1.0 \times 10^{-8}$
15	$2.88 \times 10^{-9}$	$1.9 \times 10^{-8}$

Here the number of g.-mols. of acetic acid formed is less than one-fifth of the number of quanta absorbed. It is possible that formation of other products occurs, but these could not be discovered or estimated, and the results must be taken to be in serious disagreement with those of Henri.

These measurements emphasise the need for reinvestigation of older results on the ratio of the number of molecules reacting to the number of quanta absorbed in photochemical reactions. Correcting the tables of such reactions examined from this point of view which were presented to the Faraday Society in October, 1925 (Allmand, Dhar, and Mukerji), we now find that in 65% of the cases the number of molecules reacting is, within a factor of about 3, equal to the number of molecules physically activated, indicating fairly simple mechanisms in all these examples. In 20% of the cases, chiefly those involving halogen molecules, the number of molecules changed is many times the number of quanta absorbed, indicating "chain" mechanisms. It is characteristic

of this class of reaction that "inhibitors" produce their large effect by interfering with the "chains." In 15% of the cases, the number of molecules reacting is much less than the number of quanta absorbed, and in some of these cases, again involving the halogens, we find long lives of activated molecules (Briers, Chapman, and Walters, this vol., p. 562; Eggert, *Physikal. Z.*, 1925, 26, 865), and reaction rates varying with the square root of the light absorbed (Bodenstein and Lütkemeyer, *Z. physikal. Chem.*, 1924, 114, 208; Berthoud and Bellenot, *J. Chim. phys.*, 1924, 21, 308), all indicating a primary dissociation of the halogen molecule, followed by extensive slow recombination of the atoms produced, only an occasional atom entering into the observed chemical change. There is need for much work to elucidate the complexities of these last two classes of reactions. It is significant, however, that the first class of reactions should be the largest; here apparently every molecule physically activated takes part in chemical change, showing that under these conditions, when a molecule is activated, its chemical reactivity on collision is not affected by its orientation.

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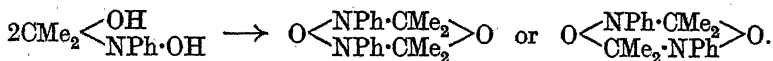
## CCXI.—The Constitution of the Condensation Product of $\beta$ -Phenylhydroxylamine and Acetone.

By FRANCIS HARROLD BANFIELD and JOSEPH KENYON.

A CONCENTRATED solution of  $\beta$ -phenylhydroxylamine in acetone deposits, after about two weeks, large, rhombic crystals which melt at 136°. To this compound Bamberger and Rudolf, who first described it (*Ber.*, 1907, 40, 2237), gave the constitution  $\text{Me}_2\text{C} \begin{array}{c} \diagup \text{NPh} \\ \diagdown \text{O} \end{array}$  by analogy with  $\text{PhCH} \begin{array}{c} \diagup \text{NPh} \\ \diagdown \text{O} \end{array}$ ,\* at that time regarded as the constitution of the condensation product of  $\beta$ -phenylhydroxylamine and benzaldehyde. Beckmann and Scheiber (*Annalen*, 1907, 355, 235) showed, by molecular-weight determinations, that the empirical formula must be doubled, and prepared analogous

\* Bamberger subsequently (*Ber.*, 1922, 55, 3376; 1924, 57, 2082) replaced this formula by  $\text{PhCH:NPh:O}$  in accordance with the modern formulation of azoxy-compounds, and support for the new constitution is afforded by the formation of the additive compound  $\begin{array}{c} \text{CHPh:NPh} \\ | \\ \text{NPh-CO} \end{array} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array}$  with phenylcarbimide.

compounds from acetone and  $\beta$ - *p*- and *m*- (but not *o*-) tolyl- and  $\beta$ -( $\alpha$ -naphthyl)-hydroxylamines. They did not succeed, however, in preparing condensation compounds when acetone was replaced by its homologues. Scheiber and Wolf (*Annalen*, 1908, 357, 25), who studied the reaction products of acetone and these  $\beta$ -aryl-hydroxylamines in some detail, suggested that the condensation is due to loss of water following direct combination of the two reagents; *e.g.*,



They did not, however, prepare any crystalline derivatives or well-defined decomposition products in support of either of these formulæ.

Although, as stated by Scheiber and Wolf (*loc. cit.*), the condensation product of  $\beta$ -phenylhydroxylamine and acetone is very susceptible to acidic reagents, yet it is possible by working under carefully regulated conditions to prepare a number of its crystalline derivatives and other definitely characterised products. The formation of these is in no way accounted for by the formulæ given above.

The maximum yield of the condensation product—68%—is obtained by the interaction, at the ordinary temperature, of dry  $\beta$ -phenylhydroxylamine and acetone during a period of two to three months. Reaction at a higher temperature results in rapid decomposition of the  $\beta$ -phenylhydroxylamine, and the effect of adding calcium chloride or sodium sulphate to the reaction mixture to combine with the liberated water is to diminish the yield of the condensation product.

The filtrate after removal of the condensation product consists of two layers: (a) water, (b) an acetone solution of azoxybenzene and aniline. The latter two substances are the normal decomposition products of  $\beta$ -phenylhydroxylamine and can be isolated in amounts almost sufficient to account for the portion of the  $\beta$ -phenylhydroxylamine which does not condense with acetone. The probable course of the reaction between acetone and  $\beta$ -phenylhydroxylamine may therefore be represented by the equation  $2\text{Me}_2\text{CO} + 2\text{PhNH}\cdot\text{OH} = \text{C}_{13}\text{H}_{22}\text{O}_2\text{N}_2 + 2\text{H}_2\text{O}$ .

The condensation product decomposes slowly in solution at the ordinary temperature; when a solution in 96% alcohol is boiled for 24 hours, complete decomposition into mesityl oxide, aniline, and azoxybenzene occurs.

The condensation product reacts readily at the ordinary temperature with acetic anhydride to yield a crystalline *monoacetyl*

derivative,  $C_{20}H_{24}O_3N_2$ , and in pyridine solution with benzoyl chloride to give a crystalline *monobenzoyl* derivative,  $C_{25}H_{26}O_3N_2$ . These results alone suffice to show the incorrectness of the formulæ mentioned above, since none of them contains a reactive hydrogen atom which would be likely to undergo displacement by an acyl group. The acyl derivatives are readily and quantitatively converted into the original condensation product on hydrolysis and therefore are very probably derivatives of it and not of some transformation compound.

The introduction of an acyl group into the molecule of the condensation product renders it resistant to permanganate and other oxidising agents and to dilute acids—including acetic acid—which attack it readily. The acyl group evidently protects a very reactive portion of the molecule, and since it can be removed by warming for a few minutes with alcoholic potash, there is a strong presumption that the group so protected is a hydroxyl group. Additional evidence for the presence of a hydroxyl group is afforded by the production at the ordinary temperature of a *potassium* derivative,  $C_{18}H_{21}O_2N_2K$ , which reacts with benzoic anhydride to give the benzoyl derivative described above. That the hydroxyl group is attached to nitrogen is rendered probable by the ease with which this potassium derivative is quantitatively oxidised by air to a red compound,  $C_{18}H_{21}O_2N_2$  (see p. 1622).

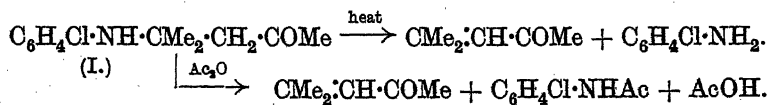
*Action of Dilute Hydrochloric Acid on the Condensation Product.*—The finely-powdered material is readily decomposed by dilute hydrochloric acid, the principal product being a liquid base,  $C_{12}H_{16}ONCl$ ; small quantities of azobenzene,  $\beta$ -phenylhydroxylamine and *p*-chloroaniline and a trace of mesityl oxide are also produced. This base differs in composition from the original compound by  $C_6H_6ONCl$ , and this fact and the nature of the by-products indicate that one of the  $\beta$ -phenylhydroxylamine residues has been detached from the compound during the reaction. Moreover, the acquisition of a chlorine atom under such mild treatment is in harmony with the view that a hydroxyl group attached to a nitrogen atom has been replaced by a chlorine atom:  $\cdot NPh\cdot OH + HCl \rightarrow \cdot NPhCl$ . The chloro-base thus produced does not, however, liberate iodine from an acidified solution of potassium iodide, so it is necessary to assume that the chlorine atom has already migrated into the benzene nucleus. This view is confirmed by the behaviour of the chloro-base, which decomposes into *p*-chloroaniline and mesityl oxide in molecular proportions on heating and gives equivalent quantities of *p*-chloroacetanilide and mesityl oxide by interaction with acetic anhydride. Moreover, it reacts with nitrous acid to give a yellow crystalline *nitrosoamine* (m. p. 75–76°)—a result



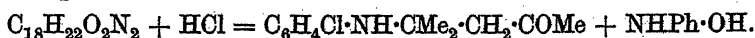
which further supports the view that the chlorine atom has wandered \* from the nitrogen atom to the nucleus.

The production of mesityl oxide and *p*-chloroaniline in equivalent proportions accounts entirely for the molecule of the chloro-base— $C_{12}H_{16}ONCl = C_6H_{10}O + C_6H_6NCl$ —and several attempts have been made, though unsuccessfully, to synthesise it from these two compounds.

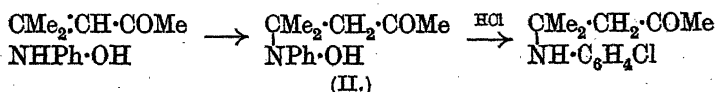
The chloro-base readily yields a crystalline *semicarbazone* ( $C_{13}H_{19}ON_4Cl$ ), the oxygen atom thus being shown to be ketonic, and by its reduction with sodium and alcohol sodium chloride and aniline are obtained in equivalent quantities together with *p*-chloroaniline and methylisobutylcarbinol. There can be little doubt, therefore, that the constitution of the chloro-base is represented by formula (I), and its modes of decomposition by heat and by acetic anhydride by the scheme :



Its formation from the original compound can be represented by the equation :



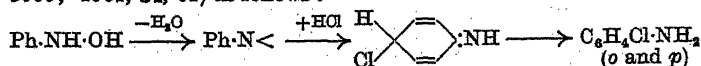
The constitution of the chloro-base as  $\beta$ -*p*-chloroanilino- $\beta$ -methyl-pentan- $\delta$ -one has been established by its synthesis from  $\beta$ -phenylhydroxylamine and mesityl oxide by the following reactions :



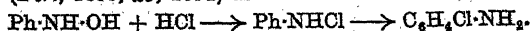
The compound (II) is too unstable to be isolated; its *sodium* derivative, however, has been prepared by the interaction of mesityl oxide and the sodium derivative of  $\beta$ -phenylhydroxylamine.

The complete and facile scission, by the action of dilute hydrochloric acid, of a molecule of  $\beta$ -phenylhydroxylamine from the original condensation product renders it probable that the latter is  $\beta$ -phenyl-

\* The mechanism of the formation of *p*-chloroaniline from  $\beta$ -phenylhydroxylamine and hydrochloric acid is represented by Bamberger (*Ber.*, 1900, 33, 3600; 1901, 34, 61) as follows :

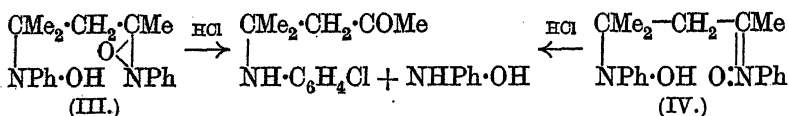


and by Löb (*Ber.*, 1896, 29, 1894) as



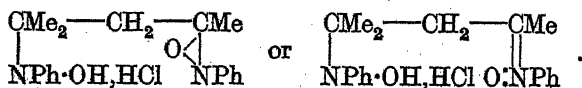
The experimental results recorded above are clearly opposed to Bamberger's view and in agreement with Löb's.

*hydroxylamino-β-methylpentan-δ-oneoxime N-phenyl ether* (III), or *β-phenylhydroxylamino-β-methylpentane-δ-phenylimine oxide* (IV), and its interaction with hydrochloric acid may be represented thus :



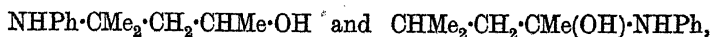
This view of the constitution of the condensation product is supported by the following additional reactions. The condensation product is rapidly decomposed by hot concentrated hydrochloric acid, giving mesityl oxide (20.5%), *p*-chloroaniline (33%) and azoxybenzene (16%) together with a small amount of a substance of very high boiling point. A similar decomposition is effected by steam, the principal products being azoxybenzene, mesityl oxide, and tarry material which has not been identified. When heated with an alcoholic solution of zinc chloride, the condensation product decomposes into *p*-phenetidine, azoxybenzene, *p*-chloroaniline, aniline and mesityl oxide. A similar scission of the molecule is brought about by the prolonged action of cold dilute sulphuric acid, the products being *p*-aminophenol, mesityl oxide and azoxybenzene; these can be isolated in amounts which account for 80% of the original material.

In marked contrast to the above-mentioned hydrolytic agents, hydrogen chloride converts the condensation product in dry ethereal solution into its *monohydrochloride*, a white solid which is decomposed by water into its components. This compound resembles β-phenylhydroxylamine hydrochloride in its behaviour and its constitution is probably



*Reduction of the Condensation Product.*—The condensation product is unaffected in moist ethereal solution by aluminium amalgam. It is, however, readily reduced in absolute alcoholic solution by sodium; aniline, azobenzene, and methylisobutylcarbinol are formed, but the main product is a secondary base,  $\text{C}_{12}\text{H}_{19}\text{ON}$ , from which a *chloroplatinate*, a yellow, crystalline *nitrosoamine*, and a *diacetyl* derivative have been prepared. Since one of the acetyl groups in this derivative is much more easily removed by hydrolysis than the other, it is probable that the secondary base contains a

hydroxyl group. Two formulæ for this compound suggest themselves :



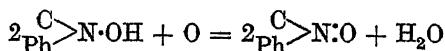
of which the former is the more probable, as it implies a decomposition of the condensation product similar to that brought about by hydrolytic agents. The alternative formula is improbable, since a compound of this structure would tend to be dehydrated by an excess of an acetylating agent.

Several unsuccessful attempts were made to synthesise the secondary base from aniline and mesityl oxide. The only definite compound which could be isolated appeared to be produced by the condensation of one molecule of mesityl oxide with two molecules of aniline.

*Action of Oxidising Agents on the Condensation Product.*—When the finely powdered condensation product is agitated with a solution of potassium permanganate, potassium ferricyanide, sodium hypobromite, or ammoniacal silver oxide, or is exposed, suspended in faintly alkaline water, to the air for several weeks, it is oxidised to a bright red, crystalline compound. The most convenient procedure, however, is by the use of ammoniacal silver oxide as described in the experimental section. The oxidised compound, which is easily obtained pure in a yield of 98% of the theoretical amount, is produced by the action of one-half molecular quantity of silver oxide, it thus being shown that only one atom of hydrogen is removed from each molecule of the condensation product. Its molecular weight is of the same order of magnitude (about 300) as that of the unoxidised compound and therefore there has been no condensation between two molecules of the latter with the elimination of hydrogen. Moreover, the two compounds are almost identical in composition and therefore no oxygen has entered the original substance. That no change other than oxidation occurs during the reaction is shown by the quantitative regeneration of the original compound by the action of aluminium amalgam on a cold moist ethereal solution of the red oxidation compound.

The oxidised and the unoxidised compound differ in several important properties. The former does not react with acetic anhydride or with benzoyl chloride in pyridine solution at the ordinary temperature, the absence of a hydroxyl group being thus indicated. This view is supported by the marked difference in the behaviour of cold dilute hydrochloric acid towards the two compounds; whereas the oxidised compound is unaffected by this reagent (and other cold dilute mineral acids), the unoxidised one

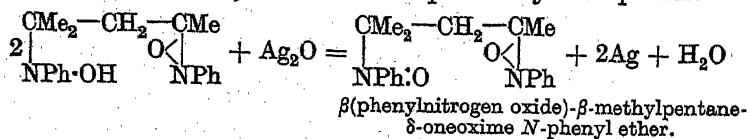
undergoes an immediate change involving the substitution of one atom of chlorine for one atom of hydrogen and one of oxygen—a type of reaction to which  $\beta$ -arylhydroxylamines are peculiarly susceptible. It is therefore probable that the oxidation process involves the reaction



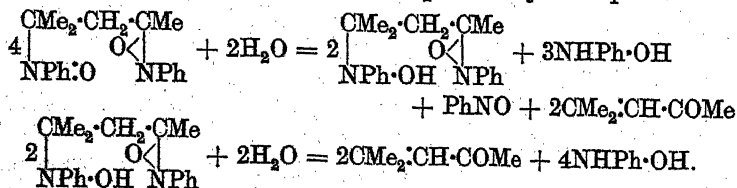
and leads to the production of a compound which contains a quadri-valent nitrogen atom.

Additional support for this view is furnished by the following experimental evidence: (a) one of the hydrolytic products of the action of dilute hydrochloric acid on the original condensation compound is  $\beta$ -phenylhydroxylamine (see p. 1623), whilst the oxidised compound in dry ethereal solution combines with hydrogen chloride to give a derivative the decomposition of which by water yields 50% of the unoxidised compound and 10% of nitrosobenzene (i.e., oxidised  $\beta$ -phenylhydroxylamine); (b) the oxidised compound is immediately decomposed by steam, giving a mixture of products from which the original unoxidised compound (22%) and nitrosobenzene (13%) can be isolated; (c) when the oxidised compound is gently heated under diminished pressure, it decomposes and nitrosobenzene sublimes from the reaction products.

Since both the unoxidised and the oxidised compound yield under the action of hot dilute mineral acids, or even of hot water, considerable quantities of mesityl oxide, the structural similarity of the aliphatic portions of the two molecules is confirmed. The oxidation process may therefore be expressed by the equation



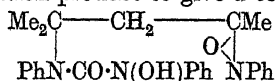
and the decomposition of the two compounds by the equations



The experimental results so far recorded do not enable a decision to be made between the oxime-ether and the nitron formulations of the condensation compound. The following results are in harmony with the first view, but since the evidence is of a negative

character the question is not considered settled. Attempts are being made to obtain further evidence on this point.

The condensation product forms an additive compound with phenylcarbimide (1 mol.)—a result which is not obtained with either its acetyl derivative or its oxidation product. All the experimental evidence points to these two derivatives having the same molecular structure as the parent compound with the sole modification that a  $>\text{N}\cdot\text{OH}$  group has been converted in the one case into  $>\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$  and in the other into  $>\text{N}\cdot\text{O}$ . It is highly probable, therefore, that phenylcarbimide reacts with the  $>\text{N}\cdot\text{OH}$  part of the condensation product to give a compound

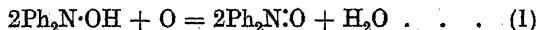


which is analogous to  $\beta$ -carbanilino- $\beta$ -phenylhydroxylamine,  $\text{NHPh}\cdot\text{CO}\cdot\text{N}(\text{OH})\text{Ph}$ , produced by the interaction of phenylcarbimide and  $\beta$ -phenylhydroxylamine (Beckmann, *J. pr. Chem.*, 1897, 56, 71).

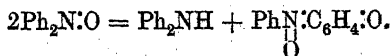
It follows also that there is present in the condensation product no other group capable of reacting with phenylcarbimide.

Evidence for the view that the condensation products of  $\beta$ -phenylhydroxylamine with acetone and with benzaldehyde differ in structure is the fact that the latter product is unaffected by cold concentrated hydrochloric acid or 65% sulphuric acid, reagents which hydrolyse the acetone compound with the greatest readiness.

One of the very few recorded cases of organic compounds which contain quadrivalent nitrogen is diphenylnitric oxide, which Wieland and Offenbächer (*Ber.*, 1914, 47, 2111) obtained by the oxidation of  $\beta\beta$ -diphenylhydroxylamine with silver oxide:



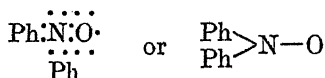
Diphenylnitric oxide is described as an intensely red substance which decomposes on keeping; liberates iodine from an acidified solution of potassium iodide; is reduced by phenylhydrazine to the original  $\beta\beta$ -diphenylhydroxylamine and by stronger reducing agents to diphenylamine; and is converted by the action of dilute hydrochloric acid, by simultaneous oxidation and reduction, into diphenylamine and quinoneanil oxide—a change which sometimes occurs spontaneously in ethereal solution (Wieland and Roth, *Ber.*, 1920, 53, 215):



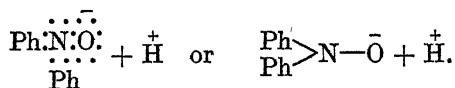
There are, therefore, many points of similarity between diphenylnitric oxide and the red compound formed by the oxidation of the

condensation product of  $\beta$ -phenylhydroxylamine and acetone, in which the presence of a quadrivalent nitrogen atom has been suggested.

The formulation of the oxidation of diphenylhydroxylamine to diphenylnitric oxide as in equation (1) is in conflict with the electronic theory. The reaction is, however, of some interest, since the oxygen atom which takes part in the reaction gains two electrons and acquires them from two molecules of the hydroxylamine. Obviously, therefore, each molecule of diphenylhydroxylamine loses one electron, and the product of oxidation has, according to the electronic theory, the formula



and can be contrasted with diphenylhydroxylamine which has "ionised":



The particular type of N—O compound formed by the oxidation of the condensation product of acetone and phenylhydroxylamine belongs, therefore, to the small class of substances whose molecules contain an uneven number of electrons—the so-called "odd electron molecules"—of which nitrogen dioxide is the most typical example; others are nitric oxide, triphenylmethyl, and chlorine dioxide. Lewis states that "odd electronic compounds" with the exception of nitric oxide absorb light in the visible part of the spectrum and are generally intensely coloured. They are very reactive and attach themselves to a great variety of substances; they tend to react in such a manner that one molecule gains an electron while another loses one (simultaneous oxidation and reduction). The red oxidation product thus appears to possess the properties of an odd electron compound, and, indeed, its method of preparation combined with the determination of its molecular weight proves that it is such a substance.

#### EXPERIMENTAL.

*Preparation of the Condensation Product.*— $\beta$ -Phenylhydroxylamine, prepared by Kamm's method ("Organic Syntheses," IV, 57) in 60% yield, was dissolved in rather more than its own weight of dry acetone, and the filtered solution was kept for several days at room temperature; the condensation product then began to

crystallise. Thereafter the mixture was kept, with daily agitation, in the ice-chest for 3 months, until no further separation occurred. The yield of the condensation product varied from 40—68% (calculated on the amount of  $\beta$ -phenylhydroxylamine), the better yields being obtained when carefully dried  $\beta$ -phenylhydroxylamine was used. The condensation product, after being washed with cold acetone, in which it was only slightly soluble, was obtained almost colourless. It crystallised from ethyl alcohol in hard, glassy rhombs, m. p.  $136^{\circ}$  (slight decomp.). In a typical experiment, 5704 g. of  $\beta$ -phenylhydroxylamine dissolved in acetone (6830 c.c.) gave, after several weeks, 3719 g. of the condensation product (yield 49%).

The reaction mixture, when left undisturbed and "unseeded," deposits the condensation product in large, colourless, transparent, glassy rhombs which remain colourless and retain the same melting point ( $136^{\circ}$ ) for several years. The small crystals obtained by frequent agitation of the solution slowly develop, during several months, a pale yellow colour and a slight odour: this is probably due to their retaining a small quantity of the mother-liquor.

Earlier workers state that this compound melts with decomposition. The amount of decomposition, however, is very small, for a molten sample will resolidify and then melt at a temperature only a few degrees below the original melting point; after one crystallisation from alcohol, it melts at  $136^{\circ}$ .

*The Acetyl Derivative.*—(a) To the deep brownish-orange solution obtained by shaking the finely powdered condensation product (10 g.) with pure acetic anhydride (10 c.c.) below  $35^{\circ}$ , ice is gradually added; the whole then sets to a crystalline mass. The washed and dried product (12 g.) melts at  $95$ — $97^{\circ}$ .

(b) To a solution of the condensation product (45 g.) in pyridine (60 c.c.) acetic anhydride is added (23 c.c.) at such a rate that the temperature does not rise above  $45^{\circ}$ . After a few minutes, crushed ice is added, and the crude acetyl derivative washed and dried as before (yield, about 54 g.).

The *acetyl* derivative separates from ethyl acetate, acetone, or aqueous alcohol in radiating clusters of prismatic needles, m. p.  $99$ — $101^{\circ}$ . When it is added to warm benzene a cloudy solution is produced which becomes clear on the addition of calcium chloride. This solution, when diluted with warm light petroleum, deposits stout needles. These melt at  $105$ — $106^{\circ}$  (without decomp.), but at about  $140^{\circ}$  vigorous decomposition sets in and tarry products are formed (Found in material crystallised from alcohol: C, 66.95; H, 7.2; N, 7.7;  $\text{CH}_3\cdot\text{CO}$ , 12.6.  $\text{C}_{20}\text{H}_{24}\text{O}_3\text{N}_2\cdot\text{H}_2\text{O}$  requires C, 67.0; H, 7.3; N, 7.8;  $\text{CH}_3\cdot\text{CO}$ , 12.0%. Found in material crystallised

from benzene: C, 71.0; H, 7.1; *M*, cryoscopic in benzene, 310.  $C_{20}H_{24}O_3N_2$  requires C, 70.6; H, 7.1%; *M*, 340).

The acetyl derivative was recovered unchanged after 1 g. had been heated with acetic anhydride (3 c.c.) at 100° for 10 minutes.

*The Benzoyl Derivative.*—(a) A solution of the condensation product (12 g.) and benzoyl chloride (6 g.) in pyridine (50 c.c.) is, after several hours, mixed with crushed ice. The washed and dried crystalline product, m. p. 90–95°, is obtained in almost quantitative yield.

(b) A suspension of the potassium derivative of the condensation product (see below) in pure dry ether is shaken with benzoic anhydride (1 mol.) for 15 minutes, the gelatinous precipitate of potassium benzoate filtered off and washed with dry ether, and the filtrate concentrated; the benzoyl derivative is thus obtained as an orange oil which solidifies completely on inoculation.

The *benzoyl* derivative crystallises from aqueous alcohol in rosettes of glistening, prismatic needles, m. p. 96–98°, containing  $1H_2O$  (Found: C, 71.0; H, 6.9; N, 6.6.  $C_{25}H_{26}O_3N_2 \cdot H_2O$  requires C, 71.4; H, 6.7; N, 6.7%) and from benzene or light petroleum in anhydrous, prismatic needles, m. p. 98–99° (Found: C, 74.6; H, 6.4.  $C_{25}H_{26}O_3N_2$  requires C, 74.6; H, 6.4%).

*Hydrolysis.* To a solution of the benzoyl derivative (1.1 g.) in warm alcohol (10 c.c.), sodium hydroxide (0.2 g.) was added, followed, after 10 minutes, by water. The crystalline product, m. p. 135–136°, weighed 0.62 g. (calc., 0.78 g.) and from the concentrated acidified filtrate 0.25 g. of benzoic acid was obtained (calc., 0.32 g.).

The *potassium* derivative is prepared by adding a benzene solution of the condensation product to rather less than one atomic proportion of finely powdered potassium. The latter dissolves, hydrogen is evolved, the liquid darkens, and a white gelatinous precipitate forms. This is filtered off, washed quickly with dry benzene several times, and dried in a vacuum (Found: K, 11.7, 11.8.  $C_{18}H_{21}O_2N_2K$  requires K, 11.3%). When left for several days in a dry atmosphere, the substance (1.1 g.) develops an orange colour and, on treatment with water, gives an orange powder, m. p. about 90°. After crystallisation from alcohol, this powder is obtained in fine red needles (1.0 g.); these, alone or mixed with an authentic specimen of the red oxidation product, melt at 89–90°.

By passing hydrogen chloride into a dry ethereal solution of the condensation product, its *monohydrochloride* is obtained as a white solid which, after being washed with ether and dried in a vacuum, melts at 62–64° and at 80° undergoes vigorous decomposition



(Found: HCl, 11.1.  $C_{18}H_{22}O_2N_2 \cdot HCl$  requires HCl, 10.9%). The solid is stable in a vacuum for some hours, but on exposure to air turns black. It is decomposed by water with regeneration of the original condensation product in an almost pure condition.

*Formation of  $\beta$ -p-Chloroanilino- $\beta$ -methylpentan-8-one from the Condensation Product.*—The freshly recrystallised and finely powdered condensation product (50 g.) is shaken for 2 hours with *N*-hydrochloric acid (400 c.c.). The pale yellow solution is filtered from undissolved material (4–8 g.) and extracted three times with ether to remove azoxybenzene, mesityl oxide and a small quantity of  $\beta$ -phenylhydroxylamine. The acid solution is rendered alkaline and the precipitated bases (35–40 g.), after extraction and drying, are distilled under 15 mm. pressure. Two main fractions are obtained, (i) up to  $150^\circ$ , (ii)  $150$ – $180^\circ$ . The first contains water (if the receiver has been cooled in ice), mesityl oxide, *p*-chloroaniline, and a proportion of the higher-boiling base. The second fraction, which weighs about three times as much as the first and contains the *chloro-base*, is dissolved in ether and the solution is washed with successive small quantities of dilute hydrochloric acid; thereafter a mixture (4.8 g.) of azobenzene and azoxybenzene (1:4) is obtained from it. The hydrochloric acid solution is rendered alkaline, the precipitated *chloro-base* (20 g.) is extracted with ether and twice redistilled, and a fraction collected at  $169$ – $172^\circ/11$  mm. or at  $133$ – $136^\circ$  under the pressure attained with a mercury vapour pump. It is a golden-yellow liquid which shows no tendency to solidify (Found: C, 63.5; H, 7.3; N, 6.3; Cl, 15.7.  $C_{12}H_{16}ONCl$  requires C, 63.8; H, 7.1; N, 6.2; Cl, 15.7%). The *nitrosoamine*, obtained by means of sodium nitrite and ice-cold, dilute hydrochloric acid, crystallises from ether-petrol in rosettes of pale yellow needles, m. p.  $75$ – $76^\circ$  after softening at  $70^\circ$  (Found: N, 11.2.  $C_{12}H_{15}O_2N_2Cl$  requires N, 11.0%).

The *chloro-base* readily yields a *semicarbazone*, which crystallises from alcohol in microscopic, flat prisms, m. p.  $125^\circ$  (Found: N, 20.2.  $C_{13}H_{19}ON_4Cl$  requires N, 19.8%).

*Action of Sodium and Alcohol on the Chloro-base.*—To a solution of the base (5 g.) in warm alcohol, sodium (3 g.) is added in small pieces; a precipitate of sodium chloride forms. By working up the product in the usual way, there is obtained a non-basic fraction (1.7 g.), b. p.  $128$ – $133^\circ$ , with a camphoraceous odour; this, after treatment with semicarbazide to remove a little unreduced mesityl oxide as its semicarbazide semicarbazone (m. p.  $220^\circ$ ), distils at  $130$ – $134^\circ$  and reacts with *p*-nitrobenzoyl chloride in pyridine solution to give a crystalline *p*-nitrobenzoic ester which melts at  $24$ – $26^\circ$  either alone or when mixed with methylisobutylcarbinyl

*p*-nitrobenzoate. The basic portion of the product consists of unchanged chloro-base (0.5 g.), *p*-chloroaniline (1.0 g.), and aniline (0.9 g.). The chlorine present as sodium chloride in the aqueous portion, estimated volumetrically, is 0.36 g., corresponding to 0.93 g. of aniline. The substance therefore contains one aniline residue for each atom of chlorine present in the molecule.

*Decomposition of  $\beta$ -p-Chloroanilino- $\beta$ -methylpentan- $\delta$ -one by Acetic Anhydride.*—The chloro-base (1.5 g.) is warmed for 15 minutes with an equal weight of acetic anhydride, and the cooled reaction mixture diluted with water (60 c.c.). The crystalline solid, after being washed and dried (0.96 g.), melts at 172–174°, alone or mixed with *p*-chloroacetanilide (Found: N, 8.2. Calc.: N, 8.1%). The filtrate contains a few globules of mesityl oxide (b. p. 126–130°).

*Synthesis of  $\beta$ -p-Chloroanilino- $\beta$ -methylpentan- $\delta$ -one.*—(a) A solution of  $\beta$ -phenylhydroxylamine (168 g.) and mesityl oxide (148 g.) in just sufficient dry ether is kept for a month and then shaken for 3 hours with *N*-hydrochloric acid (400 c.c.). The acid layer is separated, extracted three times with ether, and rendered alkaline with sodium hydroxide, and the precipitated base is extracted, dried, and distilled; the principal fraction, b. p. 160–175°/15 mm., gives, after four distillations, a fraction (40 g.), b. p. 172–175°/13 mm. (Found: N, 6.3; Cl, 15.7. Calc. for  $C_{12}H_{16}ONCl$ : N, 6.2; Cl, 15.7%). During distillation the base undergoes slight decomposition into mesityl oxide and *p*-chloroaniline.

The semicarbazone, prepared in the usual manner, crystallises from alcohol in microscopic, flat prisms, m. p. 124–125°.

(b) The gelatinous sodium derivative of  $\beta$ -phenylhydroxylamine obtained from sodium (1 equiv.) and phenylhydroxylamine (20 g.) in dry ethereal solution dissolves on addition of mesityl oxide (1 mol.), heat is developed, and a precipitate slowly separates. After 10 days, this is filtered off, quickly washed with dry ether, and dried (wt. 10 g.) (Found: Na, 11.5.  $C_{12}H_{16}O_2NNa$  requires Na, 10.0%). The compound evidently contains unchanged sodium derivative of  $\beta$ -phenylhydroxylamine (Na, 17.6%). It is very hygroscopic and decomposes on standing. It is decomposed by water, and the liberated compound is converted by cold dilute hydrochloric acid into  $\beta$ -*p*-chloroanilino- $\beta$ -methylpentan- $\delta$ -one. This synthetic chloro-base yields a semicarbazone which melts at 125° either alone or when mixed with the semicarbazone of the chloro-base obtained by the action of dilute hydrochloric acid on the original condensation compound. Acetic anhydride decomposes it into mesityl oxide and *p*-chloroacetanilide.

*Behaviour of the Condensation Product.*—(a) Towards hot hydro-

*chloric acid.* A current of steam is passed into a mixture of the condensation product (100 g.) and concentrated hydrochloric acid (100 c.c.); rapid decomposition takes place and mesityl oxide (20.5 g.) distils with the steam. From the non-volatile product, *p*-chloroaniline (33 g.), azoxybenzene (16 g.), and a non-basic material of high boiling point (2 g.) are obtained.

(b) *Towards steam.* A rapid current of steam is passed over the finely powdered compound (20 g.). An oil distils with the first 6 l. of water, leaving a black tar (5 g.). The oil sets, on cooling, to a crystalline mass of azoxybenzene (9.7 g.). Extraction of the aqueous distillate yields mesityl oxide (2.5 g.).

(c) *Towards an alcoholic solution of zinc chloride.* Zinc chloride (50 g.), the condensation product (50 g.), and ethyl alcohol (250 c.c.) are heated together under reflux for 30 minutes. After cooling, the crystalline material is filtered off and recrystallised from alcohol, glistening leaflets (9.2 g.), m. p. 237–239°, of *p*-phenetidine zincchloride being obtained [Found: Zn, 15.6; Cl, 17.4; C, 46.3; H, 5.7.  $(\text{EtO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2)_2 \cdot \text{ZnCl}_2$  requires Zn, 15.8; Cl, 17.2; C, 46.6; H, 5.3%]. From the mother-liquor, aniline (2 g.), *p*-chloroaniline (10 g.), azoxybenzene\* (11.5 g.), and mesityl oxide (3 g.) are isolated. Much of the last substance is undoubtedly lost owing to its low boiling point (40°) at the pressure employed.

The zincichloride yields phenacetin when it is heated with acetic anhydride, and *p*-phenetidine hydrochloride, m. p. 236–237°, when heated with hydrochloric acid.

*Preparation of the Red Oxidation Compound.*—A mixture of the finely powdered condensation product (59.6 g.), light petroleum, b. p. 40–60° (1500 c.c.), and an ammoniacal solution of silver oxide (from 36 g. of silver nitrate) is mechanically shaken for 48 hours; oxidation commences almost at once, the petroleum solution turning bright red and metallic silver being deposited. The petroleum layer is separated from the filtered liquid, washed with water, dried, and evaporated slowly in a bath of warm water (to avoid overheating), until crystallisation sets in. The solid on the filter is washed with water until free from ammonia, air-dried, and repeatedly extracted with dry ether; the extracts are evaporated to small bulk and diluted with light petroleum until crystallisation sets in. About one-third of the oxidation product is contained in the original petroleum solution, the remainder having crystallised

\* It is stated in the literature (Meyer and Jacobson, "Organische Chemie," II, 251; Beilstein, "Organische Chemie," IV, 1335) that azoxybenzene decomposes on heating. We have found that it distils quite readily at 191°/12 mm. with only slight decomposition. The pale yellow distillate sets completely to a mass of long, hair-like needles, m. p. 35°.

and become mixed with the metallic silver. The yield is 58.4 g. (98% of the theoretical).

This substance crystallises from petroleum in compact, hemispherical clusters of bright red, glistening prisms which melt and decompose at 88–90°, producing a black liquid which does not resolidify [Found: C, 72.7; H, 7.15; N, 9.4; *M*, cryoscopic in benzene, 276 (mean of four values).  $C_{18}H_{21}O_2N_2$  requires C, 72.7; H, 7.1; N, 9.4%; *M*, 297].

Determinations of the molecular weight of the oxidised compound in acetone by the ebullioscopic method gave values ranging from 285 to 325, but little reliance can be placed upon these, as some decomposition occurred in the hot solution. After evaporation of the acetone, the residue had a strong odour of nitrosobenzene and contained crystals of the original unoxidised condensation product of m. p. 135–136°.

*Reactions of the Red Oxidation Compound.*—(a) *Reduction.* The compound in ethereal solution is quantitatively reduced to the original condensation product by (a) zinc dust and dilute caustic soda solution, (b) aluminium amalgam, (c) phenylhydrazine. The product melts at 133–136° and 136° before and after crystallisation, respectively.

By the action of potassium iodide and dilute acetic acid on an ethereal solution of the oxidation compound the original condensation product is obtained in 77% yield, the remaining material being a dark, thick oil from which nothing crystalline can be isolated.

(b) *Action of heat.* A rapid current of steam is passed over the oxidation compound (10 g.). Fusion and decomposition take place at once and nitrosobenzene (1.2 g.) passes over with the steam. From the non-volatile portion there are isolated the original condensation product (2.2 g.), azoxybenzene (2 g.), and tar. A similar decomposition is brought about at lower temperatures when a solution of the oxidation compound in acetone is heated under reflux for several hours; the original condensation product is obtained in a yield of about 50%.

(c) *Action of acylating agents.* (i) A mixture of acetic anhydride (8 c.c.) and the finely powdered oxidation compound (6 g.) is maintained at 35° for several minutes, until solution is complete. After 30 minutes, crushed ice is added to the brownish-red solution and the precipitated paste is macerated with cold water until a sandy powder (3.8 g.) with the odour of nitrosobenzene is obtained. This crystallises in colourless needles, m. p. 105–106° (from dry benzene) or 99–100° (from aqueous alcohol). Yield 50%. Analysis and mixed melting-point determinations prove that it is the acetyl

derivative of the original condensation product of m. p.  $136^{\circ}$ ; and it yields this on hydrolysis. A 50% yield of the same acetyl derivative is obtained by the action of acetyl chloride on a solution of the oxidation compound in pyridine.

In marked contrast to the behaviour of the original condensation product, which in pyridine solution readily gives an acetyl derivative in quantitative yield by the action of acetic anhydride, the oxidation compound is unacted upon under similar conditions at the ordinary or at a slightly raised temperature. At higher temperatures, profound decomposition sets in and unworkable tars are produced. This result clearly indicates that some prior reaction is necessary before acetylation can take place.

In a similar manner, by the action of benzoyl chloride (3 g.) on a pyridine (40 c.c.) solution of the oxidation compound (6 g.), there is obtained the benzoyl derivative of the original condensation product in 50% yield; m. p. and "mixed" m. p.  $97-99^{\circ}$ .

(d) *Action of hydrogen chloride.* Dry hydrogen chloride is rapidly absorbed by a dry ethereal solution of the oxidation compound, and an orange precipitate separates; the solution becomes colourless, but slowly turns green. If the passage of hydrogen chloride is still continued, nitrosobenzene and mesityl oxide can be isolated from the solution; but if the current is stopped when the solution becomes colourless, and the orange precipitate rapidly filtered off, washed with dry ether, and dried in a vacuum desiccator, it has the empirical formula  $C_{18}H_{21}O_2N_2 \cdot 2HCl$ . This substance is not identical with the monohydrochloride of the original condensation product (*vide* p. 1622), but it yields this product in nearly 50% yield on treatment with water.

*Action of Phenylcarbimide on the Condensation Product.*—A solution of the condensation product (9 g.) and phenylcarbimide (3.3 g.; 1 mol.) in dry ether is gently warmed for 3 hours and the ether is then evaporated. The residue of colourless, cubic crystals, coated with red oil, is washed with small quantities of cold light petroleum and recrystallised from acetone, transparent, colourless cubes, m. p.  $128-129^{\circ}$  (decomp.), being thus obtained (Found: C, 71.8; H, 7.0; N, 9.7.  $C_{25}H_{27}O_3N_3$  requires C, 71.8; H, 6.5; N, 10.0%). This substance is almost insoluble in cold alcohol and decomposes slightly in hot alcohol. A mixture of it with the original condensation product (m. p.  $136^{\circ}$ ) melts at  $104-109^{\circ}$ .

*Preparation of the Liquid Reduction Product.*—To a solution of the condensation compound (60 g.) in boiling absolute ethyl alcohol (500 c.c.), sodium (23 g.) is added sufficiently quickly to keep the liquid boiling. When all the sodium has dissolved, water is added to the dark red reaction mixture and the solution is

extracted several times with ether. The ethereal solution is washed with water, extracted with dilute hydrochloric acid, and evaporated to dryness; the residue is pure azobenzene. The basic material in the acid extract is recovered and repeatedly fractionally distilled under diminished pressure, being thus separated into aniline and the new *base* (15 g.), a golden-yellow, somewhat viscous liquid, b. p.  $130-133^{\circ}/2-4$  mm. or  $160-163^{\circ}/15$  mm.,  $d_4^{25}$  1.0043 (Found: C, 74.8; H, 9.6; N, 7.3.  $C_{12}H_{10}ON$  requires C, 74.6; H, 9.8; N, 7.25%).

Modifications of the method of reduction were tried with the object of preventing the formation of azobenzene. These included the gradual addition of sufficient acetic acid to neutralise the sodium ethoxide as it was produced—this procedure, however, caused the production of phenylcarbylamine, which was very difficult to remove on distillation. The presence of water—even 1%—in the alcohol diminishes the amount of base produced and increases the proportion of azobenzene formed even to the exclusion of the base when the quantity of water is considerable. When the absolute alcohol is replaced by amyl alcohol, no base is formed, an almost quantitative yield of azobenzene \* being obtained together with a trace of aniline.

By doubling the amount of sodium used in the reduction, there was produced, in addition to the liquid base, hydrazobenzene (5 g.), which was isolated from the acid extract in the form of benzidine.

The pure base readily yields a *diacetyl* derivative, which crystallises from acetone in clusters of prismatic needles, m. p.  $104-106^{\circ}$  (Found: N, 4.9;  $2CH_3\cdot CO$ , 31.8;  $1CH_3\cdot CO$ , 19.0.  $C_{16}H_{23}O_3N$  requires N, 5.05;  $2CH_3\cdot CO$ , 31.1;  $1CH_3\cdot CO$ , 15.5%). When the hydrolysis is effected by aqueous potassium hydroxide, a value for the acetyl content of 19% is quickly obtained; this value increases at only a slow rate as the heating is continued—the maximum value of 31.1% was only obtained by heating with *alcoholic* potassium hydroxide during 24 hours. It is evident, therefore, that one acetyl group is much more firmly attached than the other.

The *chloroplatinate* of the base is obtained by the addition of chloroplatinic acid (1 mol.) in alcoholic solution. The precipitate crystallises from methyl alcohol containing a small amount of hydrochloric acid in clusters of orange prisms which, after drying at  $110^{\circ}$  for 4 hours, melt and decompose at  $197-198^{\circ}$  [Found: Pt, 24.9, 24.6.  $(C_{12}H_{10}ON)_2\cdot H_2PtCl_6$  requires Pt, 24.5%].

The *nitrosoamine*, prepared by the addition of sodium nitrite to

\* It is somewhat remarkable that azobenzene is reduced by sodium and boiling ethyl alcohol only with great difficulty.

a solution of the base in cold hydrochloric acid, crystallises from ether in fine, pale yellow needles, m. p. 44–48° (Found: N, 12.8.  $C_{12}H_{18}O_2N_2$  requires N, 12.6%).

One of the authors (F. H. B.) is indebted to the Advisory Council of the Department of Scientific and Industrial Research for a grant which enabled this work to be carried out. The authors wish to thank Mr. P. S. Arup, M.Sc., for assistance in the early stages of the investigation.

BATTERSEA POLYTECHNIC, S.W. 11. [Received, February 23rd, 1926.]

## CCXII.—*The Classification of the Sugars.*

By JOHN GWILLIAM MALTBY.

THE original classification of the normal forms of the sugars and their derivatives into the *d*- and *l*-series was that of Fischer (*Ber.*, 1894, 27, 3208) and depended on their chemical relationship to naturally occurring (*d*-)glucose. The classification usually adopted to-day is that of Rosanoff (*J. Amer. Chem. Soc.*, 1906, 28, 114) in which the configuration of the asymmetric group furthest removed from the aldehydic group is the deciding factor. A classification depending on the mean of the rotations of the  $\alpha$ - and  $\beta$ -forms was put forward in an earlier paper (*J.*, 1922, 121, 2608).

Most sugars and their derivatives are obtainable in  $\alpha$ - and  $\beta$ -forms, and the usually accepted distinctions between them are those given by the action of enzymes, the mode of preparation and the rate of hydrolysis of the glucosides. A different distinction has been given by Hudson (*J. Amer. Chem. Soc.*, 1909, 31, 66) based on their rotations and on Fischer's classification into the *d*- and *l*-series. According to this, the  $\alpha$ -form of a *d*-sugar has a more positive rotation than the  $\beta$ -form. In the case of arabinose, however, the two methods of distinction do not agree (Hudson, *J. Amer. Chem. Soc.*, 1924, 46, 2591), the same being the case if Rosanoff's classification is used. It seems possible that the cause of the discrepancy lies in the classification into the *d*- and *l*-series being wrong.

It is suggested that, for the normal forms of the aldoses, the configuration of the middle group of the oxide ring (group 3) is the deciding factor in the classification into the *d*- and *l*-series. Naturally occurring arabinose therefore now belongs to the *d*- instead of to the *l*-series, and the  $\alpha$ -forms of the *d*-sugars have more positive rotations than the  $\beta$ -forms for all known cases, as shown in the table below. In an earlier paper (*J.*, 1923, 123, 1404), it was suggested from a consideration of the rotations of the sugars,

that, in the  $\alpha$ -form of the aldoses, groups 1 and 3 have opposite configurations. It was also shown that the configuration of group 3 determines the relative proportions of the two products formed by the cyanohydrin synthesis. This follows, since the configuration of group 2 in the main product is always the opposite of that of group 4, the latter being group 3 in the original sugar. This is also shown in the table below, in which the configurations are represented by + and - signs as suggested by Fischer (*Ber.*, 1894, 27, 3189) and the *d*-sugars have been taken as those with a positive sign for group 3.

Sugar.	Configuration of sugar.				Specific rotation of sugar.			Configuration of main cyanohydrin product.				
	5.	4.	3.	2.	$\alpha$ .	Equil.	$\beta$ .	6.	5.	4.	3.	2.
<i>d</i> -Glucose .....	-	-	+	-	100°	52°	20°	-	-	+	-	-
<i>d</i> -Mannose .....	-	-	+	+	30	14	-15	-	-	+	+	-
<i>d</i> -Galactose .....	-	+	+	-	140	80	51	-	+	+	-	-
<i>d</i> -Arabinose ...		+	+	-	150	105	76		+	+	-	-
<i>d</i> -Xylose .....		-	+	-	92	19	-20		-	+	-	-
<i>d</i> -isoRhamnose	-	-	+	-	73	30	-					
<i>l</i> -Ribose .....		-	-	-					-	-	-	+
<i>l</i> -Rhamnose ...	+	+	-	-	-7	9	54	+	+	-	-	+
<i>l</i> -Fucose .....	±	-	-	+	-112	-77	-					

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### CCXIII.—The Unsaponifiable Matter from the Oils of *Elasmobranch Fish*. Part I. A Contribution to the Study of the Constitution of Squalene (Spinacene).

By ISIDOR MORRIS HEILBRON, EDWARD DAVID KAMM, and  
WILLIAM MORGAN OWENS.

THE first mention of the occurrence of squalene in fish-liver oils is due to Tsujimoto (*J. Chem. Ind. Tokio*, 1906, 9, 953), who subsequently described its physical characteristics and assigned to it the molecular formula  $C_{30}H_{50}$  (*J. Ind. Eng. Chem.*, 1916, 8, 889; 1920, 12, 63). The hydrocarbon was found to yield a well-defined crystalline hexahydrochloride, but of indefinite melting point, sintering at about 112° and finally melting to a clear liquid at about 125°. Meanwhile, in 1915, A. Chaston Chapman, working independently, isolated from fish-liver oils obtained from Portugal what would appear to be the same hydrocarbon, for which he proposed the name spinacene, and assigned to it the same molecular formula (*J.*, 1917, 111, 56). Later (*J.*, 1918, 113, 458), from the



results of other analyses of the hexahydrochloride and hexahydrobromide and of molecular-weight determinations, he concluded that its constitution was in better accord with the formula  $C_{29}H_{48}$ . This author also remarked on the indefinite nature of the melting point of the hydrochloride. He found that whereas the crude compound commenced to shrink at  $100^\circ$  and began to melt at  $110^\circ$  (Cl, 33.8%),\* after purification by means of benzene and alcohol, the final preparation became pasty at  $120^\circ$  and melted to a clear liquid at  $126^\circ$  (Cl, 34.5%). In a recent communication by André and Canal (*Compt. rend.*, 1925, 181, 612), an account is given of the hydrochlorides prepared from the unsaponifiable matter of the oils of *Cetorhinus maximus* (A) and *Scymnorhinus lichia* (B). Whilst the oils from both fish had previously been examined by Tsujimoto and found to contain squalene, that from the latter has been used by us and was also almost certainly employed by Chapman (*Analyst*, May, 1917). From A, André and Canal separated two hydrochlorides:  $A_1$ , m. p.  $107-108^\circ$  (Cl, 35.3%, corresponding with a hydrocarbon  $C_{28}H_{46}$ ); and  $A_2$ , m. p.  $144-145^\circ$  (Cl, 33.9%, indicating  $C_{30}H_{50}$ ). On the other hand, they obtained from B the hydrochlorides  $B_1$ , m. p.  $107-108^\circ$  (Cl, 33.9%), and  $B_2$ , m. p.  $143-145^\circ$  (Cl, 33.2%), the latter chlorine content corresponding to the hydrocarbon  $C_{31}H_{52}$ . A mixture of  $A_1$  and  $B_1$  is stated to show no depression of melting point, whilst  $A_2$  and  $B_2$  give a slight depression ( $139-140^\circ$ ). From these highly conflicting results, the authors claim that neither squalene nor spinacene is a definite chemical compound, but each is a mixture of various unsaturated hydrocarbons from which the  $C_{29}H_{48}$  homologue proposed by Chapman is apparently absent. We agree with André and Canal in so far that we have separated hydrochlorides of different melting points, but find for each the same values for carbon, hydrogen, and chlorine in strict agreement with a hydrocarbon formula  $C_{30}H_{50}$ .† It would appear that three isomeric hydrochlorides, m. p.  $107-108^\circ$ ,  $113-114^\circ$ , and  $144-145^\circ$ , exist, although it is somewhat doubtful whether the lowest-melting one is a pure compound (see experimental part). The hydrocarbon has been regenerated from each hydrochloride and reconverted into its hydrochloride, which, in every case, is again separable into low- and high-melting fractions.

	C %.	H %.	Cl %.
* $C_{28}H_{46}Cl_6$	55.9	8.7	35.4
$C_{29}H_{48}Cl_6$	56.7	8.8	34.6
$C_{30}H_{50}Cl_6$	57.2	8.9	33.9
$C_{31}H_{52}Cl_6$	57.9	9.0	33.1

† The squalene used was obtained from *Lepidorhinus squamosus*, *Etmopterus spinax*, *Centrophorus granulosus*, and *Scymnorhinus lichia*, and the material from each source gave the same results.

TABLE I.  
The Constants of Squalene.

	Chapman.	Tsujimoto.	Majima and Kubota.	Present authors.
B. p. at 0.15 mm. ....			205°	
0.55 " .....			235—237°	
2 " .....				240—242°
4 " .....				248—250°
5 " .....		252—254°		
9 " .....	260°			261—262°
10 " .....		262—264°		
15 " .....				270—275°
25 " .....				
Density .....	0.8610/ <sub>15°</sub>		284—285°	
	0.8588/ <sub>20°</sub>	0.8587/ <sub>4°</sub>	0.8596/ <sub>4°</sub>	0.8655/ <sub>15°</sub>
	0.8616/ <sub>4°</sub>		0.8584/ <sub>20°</sub>	0.8538/ <sub>20°</sub>
				0.8596/ <sub>18°</sub>
Refractive index $n_D^{15}$ ...	1.4987		1.4959, 1.4966	
$n_D^{15}$ ...				1.4972
$n_D^{20}$ ...	1.4967, 1.4951	1.4965	1.4965	1.4965, 1.4980
Mol. refraction .....	139.1, 134.5*	139.1	139.8	139.6, 139.8, 139.9
Iodine value .....	367.9			377.6
Mol. wt. (cryoscopic) .....	394, 391 (benzene)	408 (benzene)	407 (ethylene dibromide)	391 (benzene) 430 (ethylene dibromide)

\* Calculated for  $C_{30}H_{50}$ .

These results lead to the conclusion, which is also borne out by other evidence, that squalene and spinacene are one and the same hydrocarbon of the molecular formula  $C_{30}H_{50}$ . Taking into account the number of species of fish from which squalene has been isolated, we are of the opinion that no evidence has been adduced in favour of André and Canal's view (*loc. cit.*) that homologues of this hydrocarbon exist in marine animal oils. On the other hand, the isolation of the isomeric hydrochlorides would appear to indicate that squalene is itself a mixture of isomerides. In support of this view, it has repeatedly been found that the density and refractive index are not absolutely constant, although the calculated molecular refraction is almost exactly the same for different specimens. This value shows a marked exaltation ( $\Sigma[R_L]_D = 1.8-2.3$ ) over the theoretical value for  $C_{30}H_{50}$ . This exaltation is not due, however, to the presence, as André and Canal claim, of a  $C_{31}H_{52}$  homologue in squalene, for the hydrocarbon regenerated from the hexahydrochloride melting at 107—108°, which, according to these authors, corresponds to  $C_{30}H_{50}$  in the case of *Scymnorhinus lichia*, also shows exactly the same exaltation. The exaltation is apparently not due to the presence of conjugated double bonds, since we, confirming Majima and Kubota (*Jap. J. Chem.*, 1922, 1, 9), have found that squalene is inert towards sodium and boiling amyl alcohol.

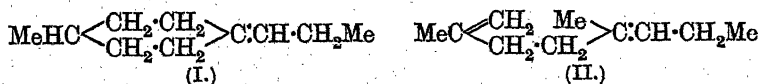
#### Sources of Squalene.

Squalene is widely distributed among elasmobranchs. It occurs chiefly in the family *Squalidae*, but is not found in every member of it. Moreover, it is not peculiar to elasmobranchs, for Drummond, Channon, and Coward (*Biochem. J.*, 1925, 19, 1047) have

reported its presence in the unsaponifiable matter of cod-liver oil. The hydrocarbon, although occurring chiefly in the liver oil, has also been found in the egg oils of *Chlamedoselachus anguineus* and *Lepidorhinus kinbei* by Tsujimoto (*loc. cit.*), and of *Etmopterus spinax*, *L. squamosus*, and *Scymnorhinus lichia* by us. Moreover, the intestines of the last-mentioned fish always contain a large amount (up to 300 c.c.) of a dark oil, the greater part of which is squalene. This may be produced *post-mortem*—the specimens when treated have always been dead for several days—but the fact that it is invariably present seems to us to favour the view that it is a characteristic of the living animal. An examination was made in May, 1925, of 115 female *E. spinax*. From some of these, eggs in a comparatively undeveloped condition were dissected, all of which contained squalene. In others, almost completely developed embryo with yolk-sac were found. The sac did not contain the hydrocarbon, which must therefore have been absorbed during the growth of the embryo. A noteworthy fact regarding squalene-containing fish is the remarkable health of their bodies, in which internal parasites are very rare (private communication from Professor Johnstone).

#### *Decomposition of Squalene by Heat.*

This has been studied by Chapman (J., 1923, 123, 769) and Majima and Kubota (*loc. cit.*). The latter investigators subjected squalene to dry distillation and obtained fractions boiling at all temperatures from 36°/760 mm. to 235°/18 mm. They claim to have identified isoprene; the constants recorded, however, are very low ( $D_D^{18}$  0.6692,  $n_D^{18}$  1.39641; compare Harries, *Ber.*, 1914, 47, 1999). From the most abundant higher fraction, a liquid,  $C_{10}H_{18}$  (b. p. 62.5–66°/17 mm.), was obtained the physical constants of which resemble those of *cyclodihydromyrcene* or *cyclodihydrolinolo-olene*. Chapman's methods of decomposition were somewhat different, but gave apparently similar products. He concludes that the low-boiling fraction is a mixture of one or more amylenes with some isoprene or isomeric substance, whilst the main products are considered to be 1-methyl-4-propylenecyclohexane (I) and the closely related diolefinic hydrocarbon (II).



By the dry distillation of squalene and careful fractionation of the product, we obtained members not only of the hemiterpene and monoterpene groups, but also of the sesquiterpene, diterpene, and probably even higher divisions of the same family.

The lowest-boiling liquid member obtained by us has been

definitely proved to be an amylene, oxidation of which by potassium permanganate yielded acetone, from which it follows that its structure must be  $\text{CMe}_2\text{:CHMe}$  (III).

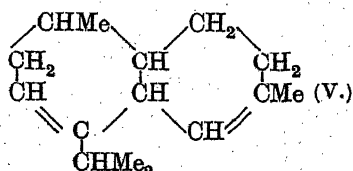
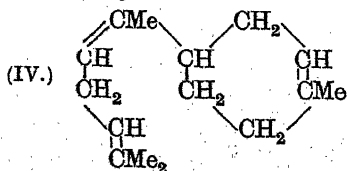
The fraction of next higher boiling point ( $62\text{--}100^\circ/20\text{ mm.}$ ), which appears to be a mixture of monoterpenes and dihydromonoterpenes, is under investigation.

The third fraction, boiling between  $120^\circ$  and  $170^\circ/20\text{ mm.}$ , consists of a complex mixture of monocyclic sesquiterpenes. By repeated distillation a constant-boiling fraction has been isolated the physical characteristics of which (Table II) are identical with those of bisabolene (Ruzicka, *Helv. Chim. Acta*, 1925, 8, 259). In addition, ring closure by means of formic acid has yielded a dicyclic isomeride the constants of which agree closely with those of the dicyclic sesquiterpenes isolated by Ruzicka from nerolidol and which, according to this author, could only have resulted through the intermediate formation of farnesene and bisabolene (Table II).

TABLE II.

	B. p./12 mm.	$d_{20}^{25}$ .	$d_4^{25}$ .	$n_D^{25}$ .	$[R_L]_D$ .
Hydrocarbon from squalene ...	129—135°	0.8734	0.8716	1.4915	67.72
Synthetic bisabolene .....	130—137	—	0.8717	1.4923	67.99
				(Calc., 67.87)	

In an attempt to obtain further evidence regarding the carbon skeleton of the entire sesquiterpene fraction, this was dehydrogenated with sulphur (compare Ruzicka, *Helv. Chim. Acta*, 1922, 5, 345), and the product distilled over sodium. In three different experiments, addition of alcoholic picric acid produced, in insufficient quantity for analysis, orange crystals of what appeared from the melting point to be cadalene picrate. The difficulty of obtaining cadalene in appreciable quantity is not peculiar to the sesquiterpene mixture handled by us, for Staudinger (*Helv. Chim. Acta*, 1922, 5, 785) failed to isolate any trace of this hydrocarbon on dehydrogenation of the sesquiterpene fraction from caoutchouc, which should most certainly have yielded it. Moreover, Ruzicka was unable to obtain cadalene from the compound (IV) (*Helv. Chim. Acta*, 1923, 6, 487), whereas it was readily obtained from cadinene (V), which is similarly constituted.



From the complex mixture of higher-boiling fractions dicyclic terpenes have been isolated, and these, on treatment with formic acid, pass into tricyclic isomerides, a reaction reminiscent of the

conversion of the monocyclic  $\alpha$ -camphorene into its tricyclic isomeride (Ruzicka, *Helv. Chim. Acta*, 1924, 7, 279). The residue, which probably consists of members of the next higher group ( $C_{25}H_{40}$ ), has not yet been examined.

### *Isomerisation of Squalene.*

In addition to the isomerism due to variation in position of one or more of the ethenoid linkings, there exists, as might have been anticipated, isomerism due to ring formation. Majima and Kubota (*loc. cit.*) were the first to prove that squalene can be so isomerised, but it is apparent from their results that they failed to obtain a pure isomeride. As shown in Table III, 95% formic acid is the best catalyst for effecting ring closure in the squalene molecule, which, we have found, cannot be cyclised beyond the stage at which two double bonds remain (Table III).

TABLE III.  
Molecular Refractions of Squalene Isomerides.

Isomerising agent.	Time in hours.	Ethenoid linkings (iodine values).	[ $R_L$ ] <sub>D</sub> .		$\Sigma[R_L]_D$ .
			Found.	Calc.	
(Pure squalene) .....	—	6	139.8	137.98	1.85
Acetic anhydride with sulphuric acid .....	2½	—	136.9	—	—
Alcoholic sulphuric acid ...	18	—	134.0	—	—
Formic acid .....	½	—	136.9	—	—
" " .....	3	3	134.3	132.6	1.7
" " .....	9	3	134.1	132.6	1.5
" " .....	24 (or longer)	2	133.2	130.9	2.3

### *Constitution of Squalene.*

At this point we would again emphasise our conviction that squalene and spinacene are identical. In addition to the evidence of the hydrochloride formation, we are led to this conclusion by the following considerations :

(a) The physical properties of spinacene as recorded by Chapman agree closely with those recorded by all other workers in the same field (Table I).

(b) The calculated molecular refraction for  $C_{29}H_{48}|_6^-$  is 133.1, not 134.3 as stated by Chapman (J., 1918, 113, 458). The value of 134.5 determined by him is in no better agreement with this than the value worked out from the same data for  $C_{30}H_{50}|_6^-$  (139.3) is with the theoretical value 137.7.

(c) It does not appear to us that evidence based on cryoscopic measurements can be considered sufficiently trustworthy to distinguish between successive homologues ( $C_{29}H_{48}$ ,  $C_{30}H_{50}$ ) of such high molecular weight.



show that the administration of squalene results in the amount of cholesterol in the liver being more than doubled. This observation may support the view that squalene is a precursor in cholesterol synthesis in the animal body; on the other hand, the large cholesterol increase may be due to some factor yet to be determined. Further biochemical work is in progress to confirm or disprove the hypothesis.

TABLE IV.

Comparison of the Products of Decomposition of Squalene and Caoutchouc.

Product.	Source.	M.	B. p.	d.	n <sub>D</sub> .	[R <sub>L</sub> ] <sub>D</sub> .	[R <sub>L</sub> ] <sub>D</sub> calc. for
C <sub>8</sub> H <sub>8</sub>	Caoutchouc		30—50°/760 mm.				
C <sub>8</sub> H <sub>8</sub>	Squalene		32—40°/760 mm.				
C <sub>10</sub> H <sub>16</sub>	Caoutchouc	142	58°/11 mm.	0.8390/20°	1.4724/20°	45.42	C <sub>10</sub> H <sub>16</sub> $\frac{1}{2}$
	Squalene		86—101°/25 mm.	0.8326/21°	1.465/21°	45.17	= 45.24
	(cyclised by HCO <sub>2</sub> H)						
C <sub>14</sub> H <sub>24</sub>	Caoutchouc	200	88—91°/0.05 mm.	0.8895/20°	1.4980/30°	67.23	C <sub>14</sub> H <sub>24</sub> $\frac{1}{2}$
	Squalene		129—135°/12 mm.	0.8734/21°	1.4915/21°	67.8	= 67.83
			152—163°/15 mm.	0.8934/16°	1.499/16°	67.04	
C <sub>20</sub> H <sub>32</sub>	Caoutchouc	268	118—122°/0.02 mm.	0.9046/20°	1.5063/20°	89.41	C <sub>20</sub> H <sub>32</sub> $\frac{1}{2}$
	Squalene		180—190°/9 mm.	0.9073/19°	1.5080/19°	89.33	= 89.7
		259	190—200°/9 mm.	0.9157/19°	1.513/19°	88.88	
—	Caoutchouc	303	142—148°/0.04 mm.	0.9161/20°	1.5119/20°	89.17	C <sub>20</sub> H <sub>32</sub> $\frac{1}{2}$
						(If C <sub>20</sub> H <sub>32</sub> ) 111.2 (If C <sub>20</sub> H <sub>30</sub> )	= 111.3

## EXPERIMENTAL.

*Extraction of Oils.*—The fish were dissected immediately on arrival, and the livers removed and weighed. The stomach was in each case ligatured and the contents were examined for the presence of oil. Any eggs in the females were separated and examined. Table V gives the oil content of the various species. The livers were cut into small pieces and the oil was extracted by heating with a coil into which steam was admitted for about  $\frac{1}{2}$  hour. The liberated oil was separated from tissue matter by means of a centrifuge and was obtained as a clear mobile liquid, pale yellow to orange in colour.

*Extraction of the Hydrocarbon from the Liver Oil.*—(a) *Saponification.* Considerable difficulty was experienced in saponifying the oil and separating the unsaponifiable matter. After many experiments, including saponifications in alcohol, it was found that the most satisfactory method was to heat the oil (500 c.c.) in a nickel basin to 105—110° and add drop by drop an equal volume of 20% sodium hydroxide solution with continuous stirring. After saponification was complete (about 1 hour), sodium chloride (150 g.) was added together with 150 c.c. of hot water. The mixture when cool was filtered through cloth, and the oil was separated from the aqueous layer, dried over sodium sulphate, and distilled at 3 mm. pressure. The squalene so obtained had a refractive index of about 1.497 and contained a small quantity of oxygenated substance (compare Chapman, J., 1917, 111, 56).

TABLE V.  
Measurements of Fish and Yield of Oil.

Fish.	Date.	No.	Sex and condition.	Length (cm.).	Wt. (g.).	Wt. of liver (g.).	Liver oil (c.c.).	Stomach oil (c.c.).	Squalene in liver oil (%).
<i>Seymourinus lichia</i> .	12.3.24	1		113	7190	1530	2000	200	Average = 55
		1		112	6270	1542	—	—	
	8.5.25	1	Male.	101	4550	840	800	150	
	12.5.25	1	Male.	125	—	2250	2000	250	
	20.5.25	5	Males.	Average = 110	—	—	1230	130	
<i>Elmopterus spinax</i> .		1	Female.	100	—	—	1000	100	50
	11.5.25	115	Mature females.	Average = 23	108	30	18	—	
<i>Centroporus granulatus</i> .	29.5.25	1	Female (after spawning).	131	—	2950	2500	—	80
<i>Lepidorhinus squamosus</i> .	1.11.24	1	Mature female.	125	—	3800	3000	—	65
		1	Female (after spawning).	123	—	1800	1500	—	
	1.5.25	5	Males.	Average = 109	—	1570	750	—	

(b) *Distillation Method*.—This method (compare Tsujimoto, *loc. cit.*) is more rapid than the preceding for the preparation of large quantities of the hydrocarbon. The oil (in portions of not more than 200 g.) was distilled under 3 mm. pressure; no distillate appeared below 235°, the major portion distilling regularly between 240° and 250°. Distillation was stopped as soon as the first signs of fuming were noticed, and an oil, containing as chief impurity a small quantity of free fatty acid, was thus obtained ( $n_D^{20}$  1.497—1.498). It was dissolved in ether, the solution, after being washed several times with dilute sodium hydroxide solution and finally with water, was dried over calcium chloride, the ether removed, and the residual oil distilled. The products ( $n_D^{20}$  1.498) thus obtained from different samples, as in the previous case, contained varying quantities of oxygen (C, 87.4, 87.2; H, 11.9, 12.0%). Pure squalene can, however, be obtained from them (a) through the hydrochloride, (b) by treatment with phthalic anhydride.

The crude hydrocarbon (160 g.) was heated for 5 hours with phthalic anhydride (18 g.) at 130—140°. After cooling and removal of unchanged anhydride, the oil in ethereal solution was shaken successively with dilute sodium carbonate and sodium hydroxide solution and washed with water. The ether was removed from the dried solution, and the residual oil distilled, the whole coming over at 260—262°/9 mm.;  $n_D^{18}$  1.4982,  $n_D^{20}$  1.4965,  $d_4^{25}$  0.8596;  $[R_L]_D$  139.6 (Found: C, 87.7, 87.7; H, 12.1, 12.0.  $C_{30}H_{50}$  requires C, 87.8; H, 12.2%).

The sodium carbonate washings contained no acid phthalate, and it must be concluded that the impurity present in the crude hydrocarbon is either a tertiary alcohol, which would seem to be closely related to the hydrocarbon, or an internal oxide similar in nature to cineole, which compound on treatment with dehydrating agents readily passes into dipentene. This point is being further examined.

Treatment of crude squalene with acetic anhydride and *d*-cam-



phorsulphonic acid also removes the impurity as a lower-boiling liquid of sharp odour. This method, however, cannot be used for the preparation of squalene, because isomerisation also occurs.

*Squalene Hexahydrochloride. General Method of Preparation.*—Dry acetone (15 g.) was saturated with dry hydrogen chloride at  $-5^{\circ}$  and squalene (5 g.) was added, the stream of gas being continued until the whole became solid; the colour of the solution changed through red to almost black. The resulting hydrochloride (6 g.) was washed free from coloured oily impurity with dry ether. By keeping the filtrate, again saturated with hydrogen chloride, in the ice-chest, a further small crop was obtained (approx. 3%). If the acetone is not presaturated with hydrogen chloride, the first crop obtained is very much smaller; the total yield, however, is only slightly diminished, as a large crop separates during the second treatment. This method is much slower and generally less satisfactory than the first. Ether also can be employed as solvent, but cannot be relied upon to give such consistent yields, being apparently sensitive to minute alteration of conditions. Analysis of the washed crude hydrochloride from any of the sources examined by us always gave similar analytical values (e.g., found: C, 57.1, 57.0; H, 9.0, 8.8%). The hydrochloride can be prepared equally readily from squalene-containing oils.

*Separation of the Isomerides. Isolation of the 107—108° Hydrochloride from Squalene obtained from Scymnorhinus lichia.*—The crude hydrochloride (14 g.), m. p. 109—112°, was digested with dry acetone (300 c.c.) for 10 minutes at  $50^{\circ}$ , boiled for one minute, and the residue (2.4 g.) filtered off. The filtrate on standing deposited hydrochloride (9.2 g.) which melted at 107—108° (Found: C, 57.2, 57.2; H, 8.8, 9.1; Cl, 33.6%). The yields of this compound, which was not always produced, varied widely even when the conditions were precisely similar. Although it appeared to be a definite isomeride, nevertheless, on digestion with hot acetone, a small residue (m. p. 111—122°) was invariably obtained.

*Isolation of the High-melting Isomeride.*—The residue (m. p. 126—130°) obtained above was combined with other sparingly soluble fractions which had been worked up in the same way. The total material (6 g.) was boiled with acetone (175 c.c.), which was then filtered quickly. The undissolved solid (2.3 g.), m. p. 140—142°, was again similarly treated with acetone (250 c.c.), and the residue (1.7 g.), now melting at about  $144^{\circ}$ , recrystallised from ethyl acetate. It formed characteristic rhombic plates, m. p. 144—145°, very similar in appearance to the 107—108° isomeride, and was practically insoluble in acetone or alcohol and moderately easily soluble in ethyl acetate (Found: C, 56.9, 56.8; H, 8.9, 8.8; Cl, 33.6, 33.8%). The intermediate portions obtained from the filtrates melted in

definitely between 111° and 120° and were separated into the high-melting hydrochloride and an isomeride, m. p. 113—114°.

The latter compound was readily prepared as follows: The washed crude hydrochloride (36 g.) was recrystallised from ethyl acetate (270 c.c.), and the separated solid (32 g., m. p. 111—120°) digested with boiling ethyl acetate. The insoluble residue (11 g., m. p. 117—130°) was now taken up in hot acetone and separated from 5 g. of undissolved material (m. p. 131—137°) by filtration. From the filtrate, crystals, m. p. 113—114°, were obtained. This compound showed no alteration in melting point on further crystallisation from acetone, in which it is moderately easily soluble, although less so than the 107—108° form (Found: C, 56.8; H, 8.9; Cl, 33.8, 33.9%).

*Regeneration of Squalene from the Hydrochlorides.*—(A) 113—114° *Isomeride*. The hydrochloride (17 g.) was boiled under reflux with pyridine (68 g.) for 4 hours in an atmosphere of carbon dioxide. The reaction mixture was poured into an excess of dilute sulphuric acid, and the hydrocarbon extracted with ether. The ethereal solution was well washed with water, dried, and, after removal of the solvent, the residual oil was distilled at 4 mm. The constant-boiling fraction was again redistilled at the same pressure, and the major portion, boiling at 240—242°, collected separately,  $n_D^{20}$  1.4990,  $d_{20}^{20}$  0.8592,  $[R_L]_D$  140.2,  $[R_L]_D$  calc. for  $C_{30}H_{50}$  137.7 (Found: C, 87.8, 87.5; H, 12.1, 12.2.  $C_{30}H_{50}$  requires C, 87.8; H, 12.2%). The regeneration can also be brought about with alcoholic sodium ethoxide, silver acetate, or quinoline. Even prolonged boiling with absolute alcohol is sufficient to effect complete decomposition of the hydrochloride.

(B) 107—108° *Isomeride*. This was similarly decomposed and the constants of the pure hydrocarbon were determined,  $n_D^{20}$  1.4955,  $d_{20}^{20}$  0.8563,  $[R_L]_D$  139.8 (Found: C, 87.6, 87.7; H, 12.3, 12.3%).

(C) 144—145° *Isomeride*. This proved slightly more difficult to decompose. The constants of the hydrocarbon after distillation over sodium were:  $n_D^{18}$  1.4990,  $d_{18}^{18}$  0.8612,  $[R_L]_D$  139.8 (Found: C, 87.4; H, 12.2%).

*Regeneration of the Hydrochlorides.*—Each of the regenerated hydrocarbons was converted into the hydrochlorides in the usual way and these, on treatment with acetone as previously described, were separated into high- and low-melting components.

*Treatment of the Oily Residues.*—After removal of the major portions of the hydrochloride, the acetone and ethyl acetate mother-liquors invariably yielded, on concentration, successive crops of lower-melting compounds (e.g., 95—96°, 84°, and 69°) and finally a sparingly soluble oil separated. That this consisted of partly decomposed hydrochloride was shown by again saturating it with

hydrogen chloride, when, on standing at  $0^{\circ}$ , the usual mixture of isomerides (m. p.  $110-116^{\circ}$ ) was again produced (Found: C, 57.0, 57.1; H, 8.9, 8.9%).

*Squalene Hexahydrobromide*.—Tsujimoto (*loc. cit.*) gives m. p.  $115-126^{\circ}$  for this compound, whilst Chapman states that, after three crystallisations from benzene, it softens at  $126^{\circ}$  and melts to a clear liquid at about  $132^{\circ}$ . Provided that the two compounds are identical, a similar discrepancy occurs in the analytical values, the results obtained by the former (C, 40.2; H, 6.4; Br, 53.0, 53.5%) being in good accord with  $C_{30}H_{50}$ , whilst Chapman's result (Br, 54.5%) agrees with  $C_{29}H_{48}$ . We have prepared this compound by the usual method (5 g. of squalene) and obtained it by recrystallisation from hot acetone in lustrous plates melting at  $118-120^{\circ}$  to a clear liquid. Although this compound has not been prepared in large quantity, a sufficient examination has been made to show that higher-melting isomerides can be obtained. The m. p. of a specimen that had been kept for 2 months in a desiccator over solid sodium hydroxide fell to  $110-113^{\circ}$ , doubtless owing to partial decomposition (Found: C, 40.1; H, 6.3; Br, 53.5, 53.7.  $C_{30}H_{50}Br_6$  requires C, 40.2; H, 6.3; Br, 53.5%).

*Isomerisation*.—(a) *Acetic anhydride containing sulphuric acid*. Squalene (150 g.) was boiled under reflux for  $2\frac{1}{2}$  hours with acetic anhydride (200 c.c.) containing 2 c.c. of sulphuric acid. The product was poured into water, neutralised with sodium carbonate, and extracted with ether. After removal of solvent from the dried solution, distillation of the residue yielded a pale yellow oil, b. p.  $253-256^{\circ}/4$  mm.,  $n_D^{20}$  1.5080,  $d_4^{20}$  0.8939,  $[R_L]_D$  136.7.

(b) *Alcoholic sulphuric acid*. Squalene (10 g.) was boiled under reflux with 50 c.c. of alcoholic sulphuric acid (15%  $H_2SO_4$ ) for 2 days. The product, after extraction as above, gave on distillation a main fraction, b. p.  $235-240^{\circ}/3$  mm.,  $n_D^{15}$  1.5049,  $d_{15}^{15}$  0.9073,  $[R_L]_D$  134.01.

(c) *Formic acid*. The hydrocarbon was boiled under reflux with twice its weight of formic acid (98%) for various periods. After cooling, the solution was diluted with water and treated as above. The products were:

*Reaction period,  $\frac{1}{2}$  hour*.—Mobile, pale yellow oil, b. p.  $215-225^{\circ}/2$  mm.,  $n_D^{15}$  1.5060,  $d_{15}^{15}$  0.8900,  $[R_L]_D$  136.8.

*Reaction period, 3 hours*.—Rather viscous, pale yellow oil, b. p.  $232-233^{\circ}/3$  mm.,  $n_D^{15}$  1.5150,  $d_{15}^{15}$  0.9207,  $[R_L]_D$  134.3, iodine value 179.9 ( $C_{30}H_{50}|_2$  requires iodine value 185.8,  $[R_L]_D$  132.6).

*Reaction period, 24 hours to 3 days*.—Very viscous, pale yellow oil, b. p.  $230-232^{\circ}/3$  mm.,  $n_D^{15}$  1.5211,  $d_{15}^{15}$  0.9359,  $[R_L]_D$  133.2, iodine value 117.4 ( $C_{30}H_{50}|_2$  requires iodine value 124.6,  $[R_L]_D$  130.9).

It will be seen that the isomerisation occurs in stages. On the assumption, which seems likely from the final results, that the

exaltation of the molecular refraction persists throughout, the product of  $\frac{1}{2}$  hour's treatment contains two rings, that of 3 hours' treatment, three rings, whilst the maximum ring closure (four) is reached after 3 days, when only two double bonds remain. For each ring formed, an increase in density and in viscosity occurs; the final product has the consistency of thick treacle, only pouring with difficulty from a test-tube at room temperature.

*Attempted Reduction of Squalene by Sodium and Amyl Alcohol.*—A mixture containing squalene (5 g.), sodium (10 g.), and amyl alcohol (20 g.) was heated to boiling, and to this, amyl alcohol was added drop by drop until all the sodium had dissolved. After treatment with water, and extraction with ether, the whole was distilled; unchanged squalene was then recovered ( $n_D^{20}$  1.5022,  $d_4^{20}$  0.8655,  $[R_L]_D$  139.85). The reaction was repeated with *n*-octyl alcohol, with the same result.

*Dry Distillation of Squalene.*—Squalene (700 g.) was distilled, in portions of not more than 150 c.c., from a 250 c.c. flask through an air condenser into another distillation flask, which served as a receiver for all high-boiling liquid. The side tube of this receiver was connected to a spiral of glass tube immersed in a freezing mixture of ice and salt, which effectively condensed the low-boiling products of the reaction. The outlet of this spiral was connected to an absorption bottle containing a 10% solution of bromine in chloroform.

During the distillation, no appreciable absorption took place, although a small quantity of a combustible gas passed through the bromine solution. The total distillate amounted to about 600 g., the residue being a polymerised resin.

The distillate was separated by fractionation into five main portions:

B. p.	Pressure.	Wt.	B. p.	Pressure.	Wt.
1. 30—45°	760 mm.	36 g.	4. 170—20°	115 mm.	110 g.
2. 60—100	20 "	224 "	5. 210—240	15 "	65 "
3. 120—170	20 "	137 "			

Fraction 1 was refractionated at atmospheric pressure, yielding (a) 28 g., b. p. 32—40°,  $n_D^{20}$  1.3940; (b) 2 g., b. p. 55—75°,  $n_D^{20}$  1.4290; (c) 4 g., b. p. above 75°,  $n_D^{20}$  1.4615.

20 G. of (a) (which was not further divisible by fractional distillation) were dissolved in cold dry carbon disulphide and treated with a 10% solution of bromine in the same solvent until the colour of the bromine just persisted after vigorous shaking and standing. After removal of carbon disulphide, the residue was distilled, and the fraction, b. p. 80—100°/20 mm., collected (yield, 35 g.). After several fractionations, a colourless liquid was obtained as the main portion, having b. p. 65—67°/13 mm.,  $n_D^{20}$  1.5140,  $d_4^{20}$  1.6773,  $[R_L]_D$  41.29 (Found: Br, by the Carius method, 72.1.  $C_5H_{10}Br_2$  requires Br, 69.6%;  $[R_L]_D$  40.84).

In order to satisfy ourselves that under precisely similar conditions isoprene yields the tetrabromo-derivative, we brominated this hydrocarbon. The product was a heavy, yellow oil, b. p. 152—156°/12 mm.,  $n_D^{20}$  1.5978, agreeing well with previously reported values for isoprene tetrabromide (Staudinger, *Helv. Chim. Acta*, 1922, 5, 765, gives b. p. 153—155°/12 mm.). Since in the case under consideration a dibromide only was formed, it is obvious that the low-boiling distillate was either a single amylene or a mixture of isomerides.

*Oxidation of the amylene.* 9 G. were shaken with a slight excess of 2½% potassium permanganate solution (23 g.  $\text{KMnO}_4$ ). After treatment with sodium bisulphite, the solution was filtered and fractionally distilled through a long column. The first 60 c.c. of the distillate were treated with *p*-nitrophenylhydrazine in hydrochloric acid and, after 12 hours, the precipitate produced was twice crystallised from dilute aqueous alcohol; yellow crystals of acetone-*p*-nitrophenylhydrazone (m. p. and "mixed" m. p. 146°) were thus obtained.

*Fraction 3* (b. p. 120—170°/20 mm.). This was distilled at 15 mm. and separated into the following fractions: (A) b. p. 110—122°, 16 g.; (B) b. p. 122—134°, 29 g.; (C) b. p. 134—144°, 40 g.; (D) b. p. 152—162°, 26 g.; (E) viscous residue.

(A) was apparently a mixture of mono- and sesqui-terpenes ( $n_D^{20}$  1.4782,  $d_4^{20}$  0.8459). Cyclisation by boiling with 98% formic acid (30 g.) for 3 hours yielded an oil which was distilled at 25 mm. into two main fractions: (1) 5 g., b. p. 86—100°,  $d_{20}^{20}$  0.8326,  $n_D^{20}$  1.4560,  $[R_L]_D$  45.17 (calc. for  $\text{C}_{10}\text{H}_{16}$ , 45.2). (2) 8 g., b. p. 130—140°,  $n_D^{20}$  1.4850.

(1) was a colourless mobile oil with an odour closely resembling that of pinene. (2) was added to sub-fraction B, which, however, further distillation indicated to be an inseparable mixture and was not further examined.

Sub-fraction C was distilled over sodium and yielded as major portion a faintly greenish-yellow oil, b. p. 129—135°/12 mm.,  $n_D^{20}$  1.4915,  $d_{20}^{20}$  0.8734,  $d_4^{20}$  0.8716,  $[R_L]_D$  67.7 (calc. for  $\text{C}_{15}\text{H}_{24}$ , 67.8). These constants are identical with those of bisabolene (Table III) (Found: C, 87.9, 87.6; H, 11.6, 11.8. Calc. for  $\text{C}_{15}\text{H}_{24}$ : C, 88.2; H, 11.8%).

20 G. of this substance were cyclised by boiling with 98% formic acid (40 g.) for 3 hours, and the product was distilled at 21 mm. and separated into: (1) 2 g., b. p. 132—135°,  $n_D^{20}$  1.4870; (2) 1 g., b. p. 137—145°,  $n_D^{20}$  1.4912; (3) 14 g., b. p. 140—145°,  $n_D^{20}$  1.4965,  $d_{20}^{20}$  0.8994,  $[R_L]_D$  66.28 (calc. for  $\text{C}_{15}\text{H}_{24}$ , 66.1).

The main fraction would appear to be very similar to one of the hydrocarbons obtained by Ruzicka (*loc. cit.*) by treating nerolidol with formic acid, the constants for which were b. p. 114—116°/12 mm.,  $d_4^{20}$  0.9069,  $n_D^{20}$  1.4964,  $[R_L]_D$  65.82.

The whole of (3) was heated with finely-powdered sulphur (5 g.) at 200—250° until no more hydrogen sulphide or mercaptan was evolved (16 hours). The volatile products of the reaction (4 g.) were distilled in a vacuum from the large amount of resinous matter produced, repeatedly distilled over sodium until colourless, and treated with a concentrated hot alcoholic solution of picric acid. After 12 hours, the deposited red oil was redissolved in alcohol. In the solution, after several weeks, there suddenly appeared yellow laminæ of picric acid mixed with long orange needles, which were mechanically separated. These commenced to shrink at 95° and melted to a clear red liquid at 108—111° (cadalene picrate has m. p. 114—115°). Similar treatment of somewhat less highly fractionated sesquiterpene products gave, on two occasions, the same orange crystals, but sufficient pure material has not yet been collected for mixed melting-point determinations with cadalene picrate.

Sub-fraction D was a somewhat more viscous and more deeply coloured oil. The constants  $n_D^{20}$  1.4990 and  $d_4^{20}$  0.8934 and the impossibility of obtaining constant-boiling fractions on redistillation indicate that it is a mixture containing a large proportion of the next fraction.

Fraction 4 (b. p. 170—210°/15 mm.). 20 G., on fractional distillation at 9 mm., gave: (A) 8 g., b. p. 180—190°,  $d_4^{20}$  0.9073,  $n_D^{20}$  1.5082,  $[R_L]_D$  89.39 (Found: C, 87.8; H, 11.6); (B) 6 g., b. p. 190—200°,  $d_4^{20}$  0.9157,  $n_D^{20}$  1.5130,  $[R_L]_D$  88.88 (Found: C, 88.0; H, 11.7; *M*, cryoscopic in benzene, 259. Calc. for  $C_{20}H_{32}$ : C, 88.2; H, 11.8%; *M*, 272.  $C_{20}H_{32}|3$  and  $C_{20}H_{32}|4$  require  $[R_L]_D$  88.76 and 90.46, respectively).

Both (A) and (B) were greenish-brown, rather viscous, and almost odourless oils. The latter seems to be identical with the compound of molecular weight 303, obtained by Staudinger (*loc. cit.*) by the distillation of caoutchouc, and assumed by him to be  $C_{25}H_{40}|4$  (see Table IV).

Treatment of (B) with boiling formic acid for 3 hours gave an isomeride, b. p. 190—200°/9 mm.,  $d_4^{20}$  0.9258,  $n_D^{20}$  1.5090,  $[R_L]_D$  87.72 (calc. for  $C_{20}H_{32}|2$ , 87.1).

Fraction 5 was a dark-coloured, viscous oil which awaits detailed examination.

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